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(54) Title: TREATMENT OF ACID GAS USING HYBRID MEMBRANE SEPARATION SYSTEMS

**(57) Abstract**

A system and method for separating acid gas from natural gas which utilizes a hybrid membrane system comprising a hydrogen sulfide membrane assembly, an acid gas membrane assembly, and, optionally, a dehydration membrane assembly. This hybrid membrane system is preferably used together with a means for converting the separated hydrogen sulfide into elemental sulfur, i.e., a Claus sulfur plant. The hydrogen sulfide membrane assembly preferably comprises a gel polymer membrane, molten salt membrane and/or rubber copolymer membrane. The acid gas membrane assembly preferably comprises a cellulose acetate membrane, polyimide membrane, polysiloxane membrane, and/or pyrolone membrane. The dehydration membrane assembly preferably comprises a polysiloxane membrane.

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# TREATMENT OF ACID GAS USING HYBRID MEMBRANE SEPARATION SYSTEMS

The present invention relates generally to the use of various hybrid membrane separation systems to separate hydrogen sulfide and carbon dioxide from natural gas feedstreams. In particular, the hybrid membrane separation systems combine an acid gas membrane system and at least one hydrogen sulfide membrane system in various configurations to provide for the separation of acid gas and concentration of hydrogen sulfide from a natural gas feedstream such that a hydrocarbon-rich retentate can be sent directly to a pipeline and wherein the resultant hydrogen sulfide-rich permeate stream is satisfactory for use in a Claus sulfur plant.

## BACKGROUND OF THE INVENTION

Mixtures of hydrogen sulfide with other gases, such as carbon dioxide and methane, are found in a number of gas streams. For example, mixtures of hydrogen sulfide, carbon dioxide, water, and methane are found in natural gases. U.S. pipeline specifications for natural gas only permit 2% carbon dioxide and 4 ppm hydrogen sulfide. Therefore, it is necessary to remove hydrogen sulfide and carbon dioxide (also referred to as "acid gas") from th gas mixtur s for the purpose of purifying th gas mixtur or r covering th

acid gas. Also, it is often necessary to purify a gaseous hydrocarbon stream to produce sweet, dry gas which will not poison certain catalysts and which can meet the usual pipeline specifications. It is also highly desirable to recover the hydrogen sulfide as a source of elemental sulfur. That is, during the separation of hydrogen sulfide from sour natural gas, it is desirable to selectively separate the hydrogen sulfide without removing all of the carbon dioxide. Usually, the separated hydrogen sulfide and a portion of the carbon dioxide are delivered to a Claus sulfur plant for conversion to elemental sulfur.

Typical natural gas processing plant flow sheets are set forth in Figs. 1 and 2, attached hereto. Fig. 1 depicts a natural gas process wherein sour natural gas is fed to a gas/liquor separation unit 10 and the resultant gaseous product is sent to an amine absorption or cryogenic fractionation unit 12 for the purpose of removing hydrogen sulfide and carbon dioxide from the gas. Amine absorption unit 12 separates the components and delivers hydrogen sulfide to Claus sulfur plant 14, carbon dioxide to compressor 16, and methane to dehydration unit 18. Claus sulfur plant 14 produces elemental sulfur which is sent to storage facility 20 and tail gases which are sent to cleanup unit 22. The methane which has been dehydrated in dehydration unit 18 is sent to nitrog n r jection unit 24 wher in helium is recovered. The methane is then compressed

in compressor 26 and the helium is sent to purification unit 28.

Fig. 2 depicts another process for carbon dioxide and hydrogen sulfide removal which is combined with acid gas enrichment. According to this process flow sheet, sour natural gas is sent to an amine absorption or cryogenic fractionation unit 30, wherein the separated acid gas comprises approximately 16% hydrogen sulfide and the remainder substantially carbon dioxide. The separated acid gas is sent to acid gas enrichment unit 32 where the hydrogen sulfide is concentrated to approximately 60% before delivery to Claus sulfur plant 34. Claus sulfur plant 34 produces elemental sulfur and residual gas which is hydrogenated (36) and separated from residual hydrogen sulfide(38) which is recycled to Claus sulfur plant 34.

Conventional methods for removing hydrogen sulfide and carbon dioxide from natural gas use amine absorption or cryogenic fractionation systems. Some examples of absorption systems used in removing acid gas from gas mixtures are set forth in U.S. Patent Nos.: 3,594,985 (Ameen et al.), which issued July 27, 1971; 4,080,424 (Miller et al.), which issued March 21, 1978; and 3,664,091 (Hegw r), which issu d May 23, 1972.

Still others have attempted to separate acid gas from natural gas by combining absorption or fractionation columns and membranes, i.e., U.S. Patent Nos. 4,374,657 (Schendel et al.), which issued February 22, 1983, and 4,466,946 (Goddin, Jr. et al.), which issued August 21, 1984.

Schendel et al. discloses a process wherein methane is first separated from a hydrocarbon feedstream by low temperature distillation, and then acid gases are separated from the remaining hydrocarbons by passing the residue through a semipermeable membrane system. The semipermeable membrane used by Schendel et al. include cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose cyanoethylate, cellulose methacrylate, or mixtures thereof.

The Goddin, Jr. et al. patent includes one embodiment wherein a process for treating a gaseous stream comprises: (a) separating a first portion of carbon dioxide from the gaseous stream in a permeation zone by selective permeation of carbon dioxide across a differentially permeable membrane to produce a carbon dioxide permeate stream and a hydrocarbon enriched first stream; and (b) further separating carbon dioxide from the hydrocarbon enriched first stream in at least one carbon dioxide removal zone by cryogenically fractionating the hydrocarbon enriched first

stream to produce at least a carbon stream and a carbon dioxide stream.

Unfortunately, the use of amine absorption or cryogenic fractionation systems for acid gas removal is extremely energy inefficient, costly and bulky. United States energy consumption for amine-based gas treatment is estimated at about 0.22 quads. Moreover, the shift in gas supply in the United States from larger gas fields to smaller, lower quality, remote gas fields will require substantially downscaled processing plants. Amine-based gas treatment systems will be economically and structurally impractical for use in these smaller fields.

Until recently, use of membrane technology for acid gas removal has not been considered for two primary reasons: (1) membranes have not been capable of separating sufficient hydrogen sulfide to reach the permissible level of 4 ppm; and (2) the composition of acid gas contains too much carbon dioxide to fit Claus sulfur plant feed specifications.

There are various known acid gas membranes which are capable of separating both carbon dioxide and hydrogen sulfide from natural gas. The membranes are disclosed in the following U.S. Patent Nos.: 4,589,896 (Chen et al.), which issued May 20, 1986; 4,659,343 (Kelly), which issued April 21, 1987; 4,435,191 (Graham), which issued March 6,

1984, and 4,857,078 (Watler), which issued on August 15, 1989. All of which are incorporated herein by reference.

Chen et al. disclose acid gas membranes such as spiral-wound cellulose acetate type or polysulfone hollow fiber type membranes. These membranes separate the bulk of carbon dioxide and essentially all the hydrogen sulfide from the hydrocarbon residual gas stream. Thereafter, the hydrogen sulfide is separated from the carbon dioxide via a fractionation column containing an acid gas removal solvent.

Kelly discloses various membranes capable of separating carbon dioxide from hydrocarbon, i.e., cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose cyanoethylate, cellulose methacrylate and mixtures thereof. Similarly, Graham discloses various polysulfone membranes which are useful for separating carbon dioxide from methane. Watler discloses a multilayer membrane comprising a microporous support onto which is coated an ultrathin permselective layer of a rubbery polymer for the separation of methane from acid gases and other hydrocarbons.

None of the aforementioned membranes are capable of adequately separating hydrogen sulfide from carbon dioxide to satisfy the Claus sulfur plant r quirements. Only the Chen et al. patent provides a step for separating hydr gen

sulfide from carbon dioxide and this step necessitates the use of a fractionation column which is economically and structurally impractical for use in smaller natural gas fields.

Several attempts at removing hydrogen sulfide from natural gas via hydrogen sulfide selective membranes are set forth in U.S. Patent Nos. 3,819,806 (Ward et al.), which issued June 25, 1974, and 4,824,443 (Matson et al.), which issued April 25, 1989. All of these patents are also incorporated herein by reference.

Ward et al. discloses an immobilized liquid membrane wherein acid gas, e.g., hydrogen sulfide, is transported therebetween due to the dissolving and dissociating of hydrogen sulfide in a water soluble salt.

Matson et al. discloses an immobilized liquid membrane made of polymers that are compatible with and swellable by a class of high boiling point, highly polar solvents containing nitrogen, oxygen, phosphorous or sulfur atoms, the swollen liquid membrane being supported either on or in the pores of other microporous supports. This membrane is capable of selective removal of the acid gases, i.e., carbon dioxide and hydrogen sulfide, from other gases and gas mixtures, and further capable of selective removal of

hydrogen sulfide in preference to carbon dioxide and carbon dioxide in preference to hydrogen.

None of the aforementioned permselective membrane systems provide a method of separating a hydrogen sulfide-rich permeate stream from natural gas sufficient for use in a Claus sulfur plant. The present inventor has develop a unique combined or hybrid membrane system which comprises both acid gas selective membranes and hydrogen sulfide selective membranes that are capable of removing acid gas from natural gas feedstreams and separating the hydrogen sulfide to a level satisfactory for use in the Claus sulfur process.

Moreover, the use of both a hydrogen sulfide selective membrane and an acid gas membrane in the removal of acid gas and separation of a hydrogen sulfide-rich permeate stream from either the acid gas or natural gas feedstreams is extremely cost effective. Such membranes can be used in downscaled processing plants or in retrofitted amine absorption systems.

Also, the membrane-based process for natural gas sweetening does not require additional energy for acid gas removal, thereby overcoming the high energy cost associated with amin absorption systems. Th use of high selective, high flux membranes will also result in minimal methane

loss. Additional advantages of such a process are: (1) low capital investment, (2) ease of installation, (3) simple operation, (4) low weight and space requirements, (5) low environmental impact, (6) highly flexible membrane system, and (7) no power, water or air is required for operation.

The present invention also provides many additional advantages which shall become apparent as described below.

## SUMMARY OF THE INVENTION

A hybrid membrane system for separating acid gas from natural gas which comprises a hydrogen sulfide membrane assembly and an acid gas membrane assembly. The hybrid membrane system according to the present invention is preferably used together with a means for converting the separated hydrogen sulfide-rich permeate into elemental sulfur, i.e., a Claus sulfur plant.

Optionally, a dehydration membrane assembly can be attached to the system for removal of water prior to delivering the hydrocarbon gas to the pipeline.

Each of the aforementioned membrane assemblies include at least one membrane module. However, two and three stage membran modules with r tentate r cycle means are preferable if a higher separation factor is desired.

Preferred membrane module designs are, for example, co-current membrane modules, counter-current membrane modules, and advantaged membrane modules. Each membrane module includes a membrane having the appropriate selectivity, i.e., hydrogen sulfide, acid gas or water. These membranes may be either spiral wound membranes, flat sheet membranes, hollow fiber membranes, plate-and-frame membranes, or any other suitable membrane configuration.

According to another embodiment of the present invention, the hybrid membrane system for separating acid gas from natural gas may also include an acid gas membrane assembly, a first hydrogen sulfide membrane assembly, and a second hydrogen sulfide membrane assembly.

Another object of the present invention is a method for separating acid gas from a natural gas feedstream which comprises: feeding the natural gas feedstream to a hydrogen sulfide membrane assembly wherein hydrogen sulfide is separated from the natural gas feedstream as a hydrogen sulfide-rich permeate; feeding the natural gas retentate from the hydrogen sulfide membrane assembly to an acid gas membrane assembly wherein a carbon dioxide-rich permeate is separated from the natural gas retentate and wherein a hydrocarbon-rich retentate is sent to a pipeline; and feeding th hydrog n sulfide-rich permeate to a means capabl of converting th hydrogen sulfid to elemental

sulfur. This method may optionally include a step of feeding the hydrocarbon-rich retentate of the acid gas membrane assembly to a dehydration membrane assembly to remove water prior to feeding the dehydrated hydrocarbon-rich retentate to a pipeline.

Another method for separating acid gas from a natural gas feedstream according to the present invention includes the steps of: feeding the natural gas feedstream to an acid gas membrane assembly wherein hydrogen sulfide and carbon dioxide are separated from the natural gas feedstream as an acid gas permeate, and wherein a hydrocarbon-rich retentate is sent to a pipeline; feeding the acid gas permeate to a hydrogen sulfide membrane assembly wherein hydrogen sulfide is separated from the acid gas permeate as a hydrogen sulfide-rich permeate; and feeding the hydrogen sulfide-rich permeate to a means capable of converting the hydrogen sulfide to elemental sulfur. The hydrocarbon-rich retentate may optionally be fed to a dehydration membrane assembly to remove water prior to feeding the dehydrated hydrocarbon-rich retentate to a pipeline.

A still further method for separating acid gas from a natural gas feedstream according to the present invention may include: feeding the natural gas feedstream to an acid gas membrane ass mbly wherein hydrogen sulfide and carbon di xid are separat d from th natural gas feedstream as an

acid gas permeate; feeding the acid gas permeate from th acid gas membrane assembly to a first hydrogen sulfide system membrane assembly wherein hydrogen sulfide is separated from the acid gas permeate as a first hydrogen sulfide-rich permeate; feeding the natural gas retentate to a second hydrogen sulfide membrane assembly wherein hydrogen sulfide is separated from the natural gas retentate as a second hydrogen sulfide-rich permeate, and wherein a hydrocarbon-rich retentate is sent to a pipeline; and feeding the first and second hydrogen sulfide-rich permeates to a means capable of converting said hydrogen sulfide to elemental sulfur. This method may optionally include a step of feeding the hydrocarbon-rich retentate of the second hydrogen sulfide membrane assembly to a dehydration membrane assembly to remove water prior to feeding the dehydrated hydrocarbon-rich retentate to a pipeline.

Any of the aforementioned systems or methods may optionally include at least one direct conversion device capable of separating residual hydrogen sulfide from the retentate of the membrane assemblies.

Other and further objects, advantages and features of the present invention will be understood by reference to the following specification in conjunction with the annexed drawings, wherein like parts have been given like numb rs.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a conventional natural gas processing plant flow sheet;

Fig. 2 shows an amine absorption and acid gas enrichment process flow sheet;

Fig. 3a is a schematic representation of a counter-current membrane module;

Fig. 3b is a schematic representation of a counter-current membrane module wherein a portion of the retentate is used as a carrier gas for the permeate;

Fig. 3c is a schematic representation of a counter-current membrane module wherein the permeate is carried out of the module by means of concentration differential;

Fig. 3d is a schematic representation of a co-current membrane module;

Fig. 3e is a schematic representation of an advantaged or natural membrane module;

Fig. 4a is a schematic representation of a two-stage membrane assembly according to the present invention;

Fig. 4b is a schematic representation of a three-stage membrane assembly according to the present invention;

Fig. 5a is a schematic representation of a combined hydrogen sulfide and acid gas membrane system in accordance with one embodiment of the present invention;

Fig. 5b is a schematic representation of a combined hydrogen sulfide and acid gas membrane system according to another embodiment of the present invention which also includes a dehydration membrane assembly;

Fig. 6a is a schematic representation of a combined acid gas and hydrogen sulfide membrane system according to another embodiment of the present invention;

Fig. 6b is a schematic representation of a combined acid gas and hydrogen sulfide membrane system according to another embodiment of the present invention which also include a dehydration membrane assembly and direct conversion means disposed throughout the system;

Fig. 7a is a schematic representation of a multiple membrane system according to still another embodiment of the present invention which comprises an acid gas membrane assembly and two hydrogen sulfide membran assemblies; and

Fig. 7b is a schematic representation of a multiple membrane system according to another embodiment of the present invention which comprises an acid gas membrane assembly, two hydrogen sulfide membrane assemblies and a dehydration membrane assembly.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides a hybrid membrane system comprising a hydrogen sulfide membrane assembly having a membrane with a high preference toward hydrogen sulfide verses carbon dioxide and an acid gas membrane assembly having a membrane with a high preference toward acid gases verses hydrocarbons and water. The hybridization of a hydrogen sulfide membrane assembly with an acid gas membrane assembly results in a system exhibiting better performance and lower construction cost than conventional absorption and cryogenic plants, especially for small plants and in the treatment of gases with high acid content. It also permits satisfactory concentration of hydrogen sulfide for use in a Claus sulfur plant, i.e., a system which converts hydrogen sulfide to elemental sulfur.

The unique hybrid membrane systems according to the present invention can best be described by reference to the attached drawings, wherein Fig. 5a depicts a hybrid m mbran system for separating acid gas from natural gas which

comprises a hydrogen sulfide membrane assembly 50 and an acid gas membrane assembly 52. This hybrid membrane system is preferably used together with a means 54 for converting the separated hydrogen sulfide-rich permeate into elemental sulfur, i.e., a Claus sulfur plant.

As shown in Fig. 5b, a dehydration membrane assembly 56 can optionally be attached to the system for removal of water prior to delivering a hydrocarbon-rich retentate to a pipeline.

Each membrane assembly 50, 52 and 56 includes at least one membrane module. As demonstrated in Figures 4a and 4b, two and three stage membrane modules with retentate recycle means are preferable if a higher separation factor is desired.

Fig. 4a depicts a membrane assembly having two membrane modules 60 and 62 attached in series. Modules 60 and 62 are connected via conduit 64 and compressor 66 wherein permeate from module 60 is delivered to module 62 under sufficient pressure to promote satisfactory separation. Retentate from membrane module 62 is preferably recycled to module 60 via recycle conduit 68. The concentrated permeate exits the two stage membrane assembly via conduit 70 in a higher concentration than the conc ntration of the permeate which xits first m mbrane module 60 via conduit 64.

Fig. 4b demonstrates a membrane assembly having three membrane modules 76, 78 and 80. Module 76 is connected to module 78 via permeate conduit 82 and compressor 84 wherein permeate from module 76 is sent to module 78 for additional separation. The retentate from module 78 is recyoled to module 76 via recycle conduit 86 for reprocessing. Similarly, module 78 is connected to module 80 via permeate conduit 88 and compressor 90 wherein permeate from module 78 is sent to module 80 for additional separation. The retentate from module 80 is recycled to module 78 via recycle conduit 92 for reprocessing. The concentrated permeate exits module 80 via conduit 94 in a much higher concentration than the original feedstream delivered to module 76.

Some of the preferred membrane module designs for use as any of the hydrogen sulfide, acid gas and dehydration membrane modules are set forth in Figures 3a-3e. Figs. 3a-3c depict various counter-current designs wherein permeate is removed from the module in a direction opposite or counter to the direction of the feedstream. That is, Fig. 3a is a counter-current membrane module wherein an inert carrier gas, e.g., nitrogen, is supplied to remove the permeate from the module. Fig. 3b utilizes a portion of the retentate to remove the permeate from the module. The permeate is removed in the counter-current membrane module

shown in Fig. 3c due to the difference in concentration in the permeate region.

Fig. 3d depicts a co-current membrane module wherein permeate is removed from the module in the same direction as the feedstream.

Fig. 3e depicts an advantaged membrane module wherein permeate is naturally or forcibly mixed to force average the concentrations.

The systems of Figs. 5a and 5b operate such that a natural gas feedstream comprising methane, carbon dioxide, hydrogen sulfide, and water, is fed to hydrogen sulfide membrane assembly 50 wherein the hydrogen sulfide-rich permeate includes hydrogen sulfide and carbon dioxide. The natural gas retentate from membrane assembly 50 includes methane, carbon dioxide and water. The hydrogen sulfide-rich permeate is delivered to a Claus sulfur plant 54 wherein the hydrogen sulfide is converted to elemental sulfur. The natural gas retentate from hydrogen sulfide membrane assembly 50 is sent to acid gas membrane assembly 52 wherein an acid gas-rich permeate and a hydrocarbon-rich retentate comprising large amounts of methane and water are produced. If the water concentration within the hydrocarbon-rich retentate m ets pipeline specifications, then the hydrocarbon-rich r tentat can be sent directly

from acid gas membrane assembly 52 to the pipeline. If, however, the water concentration exceeds pipeline specifications, then the hydrocarbon-rich retentate must be sent to a dehydration membrane assembly 56, as shown in Fig. 5b, to remove water therefrom such that a satisfactory hydrocarbon-rich feed can be sent to the pipeline.

Alternatively, the natural gas feedstream can be sent first to an acid gas membrane assembly wherein acid gases, i.e., carbon dioxide and hydrogen sulfide, are separated therefrom as an acid gas permeate which is then sent to hydrogen sulfide membrane assembly 50 (see Fig. 6a). Hydrogen sulfide membrane assembly 50 produces a hydrogen sulfide-rich permeate having a hydrogen sulfide concentration substantially higher than the acid gas permeate produced by acid gas membrane assembly 52, such that the hydrogen sulfide-rich permeate from assembly 50 can be sent to Claus sulfur plant 54 for conversion to elemental sulfur. As shown in Fig. 6b, if the hydrocarbon-rich retentate produced by acid gas membrane assembly 52 contains a water concentration great than pipeline specification, then a dehydration membrane assembly 56 may be employed. Optionally, direct conversion devices 57, 58 and 59 can be used to further reduce the amount of hydrogen sulfide contain d within the retentat from acid gas membrane assembly 52, the retentate from hydrogen sulfide membrane assembly 50, and the exhaust from th Claus sulfur plant,

respectively. These direct conversi n devices typically involve the irreversible chemical scavenging of residual hydrogen sulfide by means of well known polishing techniques.

According to another embodiment of the present invention as shown in Figs. 7a and 7b, the hybrid membrane system for separating acid gas from natural gas may also include an acid gas membrane assembly 100, a first hydrogen sulfide membrane assembly 102, and a second hydrogen sulfide membrane assembly 104. These systems operate such that a natural gas comprising methane, carbon dioxide, hydrogen sulfide and water is fed to acid gas membrane assembly 100 wherein the resultant acid gas permeate, i.e., hydrogen sulfide and carbon dioxide, is sent to a first hydrogen sulfide membrane assembly 102. The acid gas permeate is further separated in first hydrogen sulfide membrane assembly to produce a hydrogen sulfide-rich permeate having an increased concentration of hydrogen sulfide verses the acid gas permeate. The hydrogen sulfide-rich permeate is thereafter delivered to Claus sulfur plant 106 for conversion of the hydrogen sulfide to elemental sulfur. The hydrocarbon-rich retentate from acid gas membrane assembly 100, i.e., methane, water, and hydrogen sulfide, is sent to a second hydrogen sulfide membrane assembly 104 to separate most of the r sidual hydrog n sulfide contain d ther in such that the r sultant hydrocarbon-rich r tentat from m mbran

assembly 104 meets pipeline specifications. Moreover, if the hydrocarbon-rich retentate exiting second hydrogen sulfide membrane assembly 104 contains water in a quantity in excess of pipeline specification, then it may be desirable to send the hydrocarbon-rich retentate to a dehydration membrane assembly 108 to remove unwanted water therefrom.

Each membrane module preferably includes membranes having the desired selectivity, i.e., hydrogen sulfide, acid gas or water. These membranes may be either spiral wound membranes, flat sheet membranes, hollow fiber membranes, plate-and-frame membranes, or any other suitable membrane configuration.

HYDROGEN SULFIDE SELECTIVE MEMBRANES

Some examples of hydrogen sulfide selective membranes are gel polymer membranes, molten salt membranes and rubber copolymer membranes.

One example of the preferred gel polymer membrane is described in U.S. Patent No. 4,824,443 (Matson et al.), which issued on April 25, 1989, and which is incorporated herein by reference. This gel polymer membrane is a composite imm bilized liquid membrane which includes: (a) a micrqp rous support, and (b) a solvent-swoll n polymer c mpatible with and sw llable by at least one solvent

selected from a class of solvents comprising those solvents with a highly polar group in the molecular structure of the solvent, the highly polar group containing at least one atom selected from nitrogen, oxygen, phosphorous and sulfur, the solvents having a boiling point of at least 100°C and a solubility parameter of from about 7.5 to about 13.5 $(cal/cm^3-atm)^{1/2}$.

Molten salt hydrate membranes which can be used in the separation of hydrogen sulfide gas from a gaseous feedstream are disclosed in U.S. Patent No. 4,780,114 (Quinn et al.), sold by Air Products & Chemicals, Inc. of Allentown, Pennsylvania.

A rubber copolymer membrane is set forth in U.S. Patent No. 4,857,078 (Watler), which issued on August 15, 1989, and which is incorporated herein by reference. It is a multilayer membrane comprising a microporous support onto which is coated an ultrathin permselective layer of a rubbery polymer.

## ACID GAS SELECTIVE MEMBRANES

Acid gas selective membranes are preferably selected from the group consisting of: cellulose acetate membranes, polyimide membranes, polysiloxane membranes, and pyrolone

membranes. However, it is conceivable that many other polymeric membranes can also be used to separate acid gas from natural gas feedstreams.

Some examples of acid gas selective membranes are set forth in U.S. Patent No. 4,589,896 (Chen et al.), which issued May 20, 1986, U.S Patent No. 4,659,343 (Kelly), which issued April 21, 1987, and U.S Patent No. 4,435,191 (Graham), which issued March 6, 1984. Each of the aforementioned patents are incorporated herein by reference.

Illustrative polymer compositions suitable for use in acid gas membranes can be selected from polysulfone, polyethersulfone, styrenic polymers and copolymers, polycarbonates, cellulosic polymers, polyamides, polyimides, polyethers, polyarylene oxides, polyurethanes, polyesters, polyacrylates, polysulfides, polyolefins, polyvinyls and polyvinyl esters. Interpolymers, including block repeating units corresponding to the foregoing polymers, as well as graft polymers and blends of the foregoing, are also suitable for use in the membranes.

Preferred as membranes are cellulose esters, e.g., cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, c llulose cyanoethylate, cellulose methacrylate and mixtur s ther of.

DEHYDRATION SELECTIVE MEMBRANES

An example of one such dehydration selective membrane is a polysiloxane membrane manufactured by Bend Research Inc., of Bend, Oregon.

While I have shown and described several embodiments in accordance with my invention, it is to be clearly understood that the same are susceptible to numerous changes apparent to one skilled in the art. Therefore, I do not wish to be limited to the details shown and described, but intend to show all changes and modifications which come within the scope of the appended claims.

CLAIMS:

1. A hybrid membrane system for separating acid gas from natural gas which comprises:

a hydrogen sulfide membrane assembly; and

an acid gas membrane assembly.

2. The system according to claim 1 further comprising a means for converting hydrogen sulfide into elemental sulfur.

3. The system according to claim 1 further comprising a dehydration membrane assembly.

4. The system according to claim 1, wherein said hydrogen sulfide membrane assembly comprises at least one hydrogen sulfide membrane module.

5. The system according claims 4, wherein said hydrogen sulfide membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

6. The system according to claim 5, wherein said hydrogen sulfide membrane module comprises a hydrogen sulfide selective membrane selected from the group consisting of: spiral wound m mbran s, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

7. The system according to claim 6, wherein said hydrogen sulfide selective membrane is selected from the group consisting of: gel polymer membranes, molten salt membranes and rubber copolymer membranes.

8. The system according to claim 1, wherein said acid gas membrane assembly comprises at least one acid gas membrane module.

9. The system according claims 8, wherein said acid gas membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

10. The system according to claim 9, wherein said acid gas membrane module comprises an acid gas selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

11. The system according to claim 10, wherein said acid gas selective membrane is selected from the group consisting of: cellulose acetate membranes, polyimide membranes, polysiloxane membranes, and pyrolone membranes.

12. The system according to claim 3, wherein said dehydration membrane assembly comprises at least one dehydration membrane module.

13. The system according claims 12, wherein said dehydration membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

14. The system according to claim 13, wherein said dehydration membrane module comprises a dehydration selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

15. The system according to claim 14, wherein said dehydration selective membrane is a polysiloxane membrane.

16. A hybrid membrane system for separating acid gas from natural gas which comprises:

an acid gas membrane assembly;

a first hydrogen sulfide membrane assembly; and

a second hydrogen sulfide membrane assembly.

17. The system according to claim 16 further comprising a means for converting hydrog n sulfide into elemental sulfur.

18. The system according to claim 16 further comprising a dehydration membrane assembly.

19. The system according to claim 16, wherein said first and second hydrogen sulfide membrane assemblies each comprise at least one hydrogen sulfide membrane module.

20. The system according claims 19, wherein said hydrogen sulfide membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

21. The system according to claim 20, wherein said hydrogen sulfide membrane module comprises a hydrogen sulfide selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

22. The system according to claim 21, wherein said hydrogen sulfide selective membrane is selected from the group consisting of: gel polymer membranes, molten salt membranes and rubber copolymer membranes.

23. The system according to claim 16, wherein said acid gas membrane assembly comprises at least one acid gas membrane module.

24. The system according claims 23, wherein said acid gas membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

25. The system according to claim 24, wherein said acid gas membrane module comprises an acid gas selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

26. The system according to claim 25, wherein said acid gas selective membrane is selected from the group consisting of: cellulose acetate membranes, polyimide membranes, polysiloxane membranes, and pyrolone membranes.

27. The system according to claim 18, wherein said dehydration membrane assembly comprises at least one dehydration membrane module.

28. The system according claims 27, wherein said dehydration membrane module is selected from the group consisting of co-current membrane modules, counter-current membran modul s, and advantaged membrane modules.

29. The system according to claim 28, wherein said dehydration membrane module comprises a dehydration selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

30. The system according to claim 29, wherein said dehydration selective membrane is a polysiloxane membrane.

31. A method for separating acid gas from a natural gas feedstream which comprises:

feeding said natural gas feedstream to a hydrogen sulfide membrane assembly wherein hydrogen sulfide is separated from said natural gas feedstream as a hydrogen sulfide-rich permeate;

feeding the natural gas retentate from said hydrogen sulfide membrane assembly to an acid gas membrane assembly wherein carbon dioxide is separated from said natural gas retentate and wherein a hydrocarbon-rich retentate is sent to a pipeline; and

feeding said hydrogen sulfide-rich permeate to a means capable of converting said hydrogen sulfide to elemental sulfur.

32. The method according to claim 31 further comprising the step of feeding said hydrocarbon-rich retentate of said acid gas membrane assembly to a dehydration membrane assembly to remove water prior to feeding the dehydrated hydrocarbon-rich retentate to said pipeline.

33. The method according to claim 31, wherein said hydrogen sulfide membrane assembly comprises at least one hydrogen sulfide membrane module.

34. The method according claims 33, wherein said hydrogen sulfide membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

35. The method according to claim 34, wherein said hydrogen sulfide membrane module comprises a hydrogen sulfide selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

36. The method according to claim 35, wherein said hydrogen sulfide selective membrane is selected from the group consisting of: gel polymer membranes, molten salt membranes and rubber copolymer membranes.

37. The method according to claim 31, wherein said acid gas membrane assembly comprises at least one acid gas membrane module.

38. The method according claims 37, wherein said acid gas membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

39. The method according to claim 38, wherein said acid gas membrane module comprises an acid gas selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

40. The method according to claim 39, wherein said acid gas selective membrane is selected from the group consisting of: cellulose acetate membranes, polyimide membranes, polysiloxane membranes, and pyrolone membranes.

41. The method according to claim 32, wherein said dehydration membrane assembly comprises at least one dehydration membrane module.

42. The method according claims 41, wherein said dehydration membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

43. The method according to claim 42, wherein said dehydration membrane module comprises a dehydration selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

44. The method according to claim 43, wherein said dehydration selective membrane is a polysiloxane membrane.

45. A method for separating acid gas from a natural gas feedstream which comprises:

feeding said natural gas feedstream to an acid gas membrane assembly wherein hydrogen sulfide and carbon dioxide are separated from said natural gas feedstream as an acid gas permeate, and wherein a hydrocarbon-rich retentate is sent to a pipeline;

feeding said acid gas permeate to a hydrogen sulfide membrane assembly wherein hydrogen sulfide is separated from said acid gas permeate as a hydrogen sulfide-rich permeate; and

feeding said hydrogen sulfide-rich permeate to a means capable of converting said hydrogen sulfide to elemental sulfur.

46. The method according to claim 45 further comprising the step of feeding said hydrocarbon-rich retentate of said acid gas membrane assembly to a dehydration membrane assembly to remove water prior to feeding the dehydrated hydrocarbon-rich retentate to said pipeline.

47. The method according to claim 45, wherein said hydrogen sulfide membrane assembly comprises at least one hydrog n sulfid membrane module.

48. The method according claims 47, wherein said hydrogen sulfide membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

49. The method according to claim 48, wherein said hydrogen sulfide membrane module comprises a hydrogen sulfide selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

50. The method according to claim 49, wherein said hydrogen sulfide selective membrane is selected from the group consisting of: gel polymer membranes, molten salt membranes and rubber copolymer membranes.

51. The method according to claim 45, wherein said acid gas membrane assembly comprises at least one acid gas membrane module.

52. The method according claims 51, wherein said acid gas membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membran modules.

53. The method according to claim 52, wherein said acid gas membrane module comprises an acid gas selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

54. The method according to claim 53, wherein said acid gas selective membrane is selected from the group consisting of: cellulose acetate membranes, polyimide membranes, polysiloxane membranes, and pyrolone membranes.

55. The method according to claim 46, wherein said dehydration membrane assembly comprises at least one dehydration membrane module.

56. The method according claims 55, wherein said dehydration membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

57. The method according to claim 56, wherein said dehydration membrane module comprises a dehydration selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber m mbranes, and plate-and-frame membran s.

58. The method according to claim 57, wherein said dehydration selective membrane is a polysiloxane membrane.

59. A method for separating acid gas from a natural gas feedstream which comprises:

feeding said natural gas feedstream to an acid gas membrane assembly wherein hydrogen sulfide and carbon dioxide are separated from said natural gas feedstream as an acid gas permeate;

feeding said acid gas permeate from said acid gas membrane assembly to a first hydrogen sulfide system membrane assembly wherein hydrogen sulfide is separated from said acid gas permeate as a first hydrogen sulfide-rich permeate;

feeding the natural gas retentate to a second hydrogen sulfide membrane assembly wherein hydrogen sulfide is separated from said natural gas retentate as a second hydrogen sulfide-rich permeate, and wherein a hydrocarbon-rich retentate is sent to a pipeline;

feeding said first and second hydrogen sulfide-rich permeates to a means capable of converting said hydrogen sulfide to elemental sulfur.

60. The method according to claim 59 further comprising the step of feeding said hydrocarbon-rich retentate of said second hydrogen sulfide membrane assembly to a dehydration membrane assembly to remove water prior to feeding the dehydrated hydrocarbon-rich retentate to said pipeline.

61. The method according to claim 59, wherein said hydrogen sulfide membrane assembly comprises at least one hydrogen sulfide membrane module.

62. The method according claims 61, wherein said hydrogen sulfide membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

63. The method according to claim 62, wherein said hydrogen sulfide membrane module comprises a hydrogen sulfide selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

64. The method according to claim 63, wherein said hydrogen sulfide selective membrane is selected from the group consisting of: gel polymer membranes, molten salt membranes and rubber copolymer membranes.

65. The method according to claim 59, wherein said acid gas membrane assembly comprises at least one acid gas membrane module.

66. The method according claims 65, wherein said acid gas membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

67. The method according to claim 66, wherein said acid gas membrane module comprises an acid gas selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

68. The method according to claim 67, wherein said acid gas selective membrane is selected from the group consisting of: cellulose acetate membranes, polyimide membranes, polysiloxane membranes, and pyrolone membranes.

69. The method according to claim 60, wherein said dehydration membrane assembly comprises at least one dehydration membrane module.

70. The method according claims 69, wherein said dehydration membrane module is selected from the group consisting of co-current membrane modules, counter-current membrane modules, and advantaged membrane modules.

71. The method according to claim 70, wherein said dehydration membrane module comprises a dehydration selective membrane selected from the group consisting of: spiral wound membranes, flat sheet membranes, hollow fiber membranes, and plate-and-frame membranes.

72. The method according to claim 71, wherein said dehydration selective membrane is a polysiloxane membrane.

73. The method according to any of claims 31, 45 or 59, wherein residual hydrogen sulfide is separated from the retentate of any membrane assembly by means of direct conversion.

74. The system according to any of claims 1 or 16, further comprising at least one direct conversion device capable of separating residual hydrogen sulfide from the retentate of any membrane assembly.

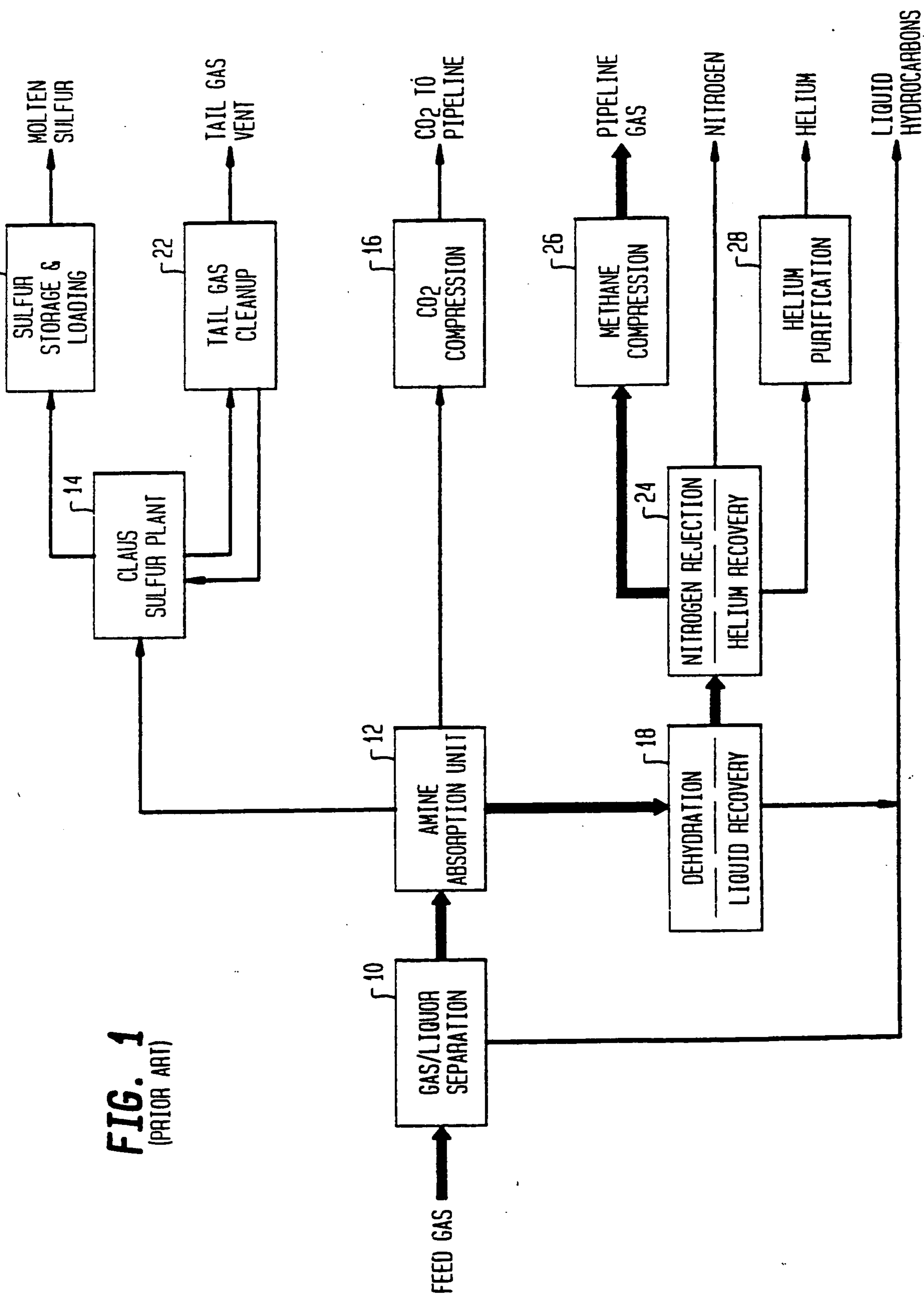



FIG. 1
(PRIOR ART)

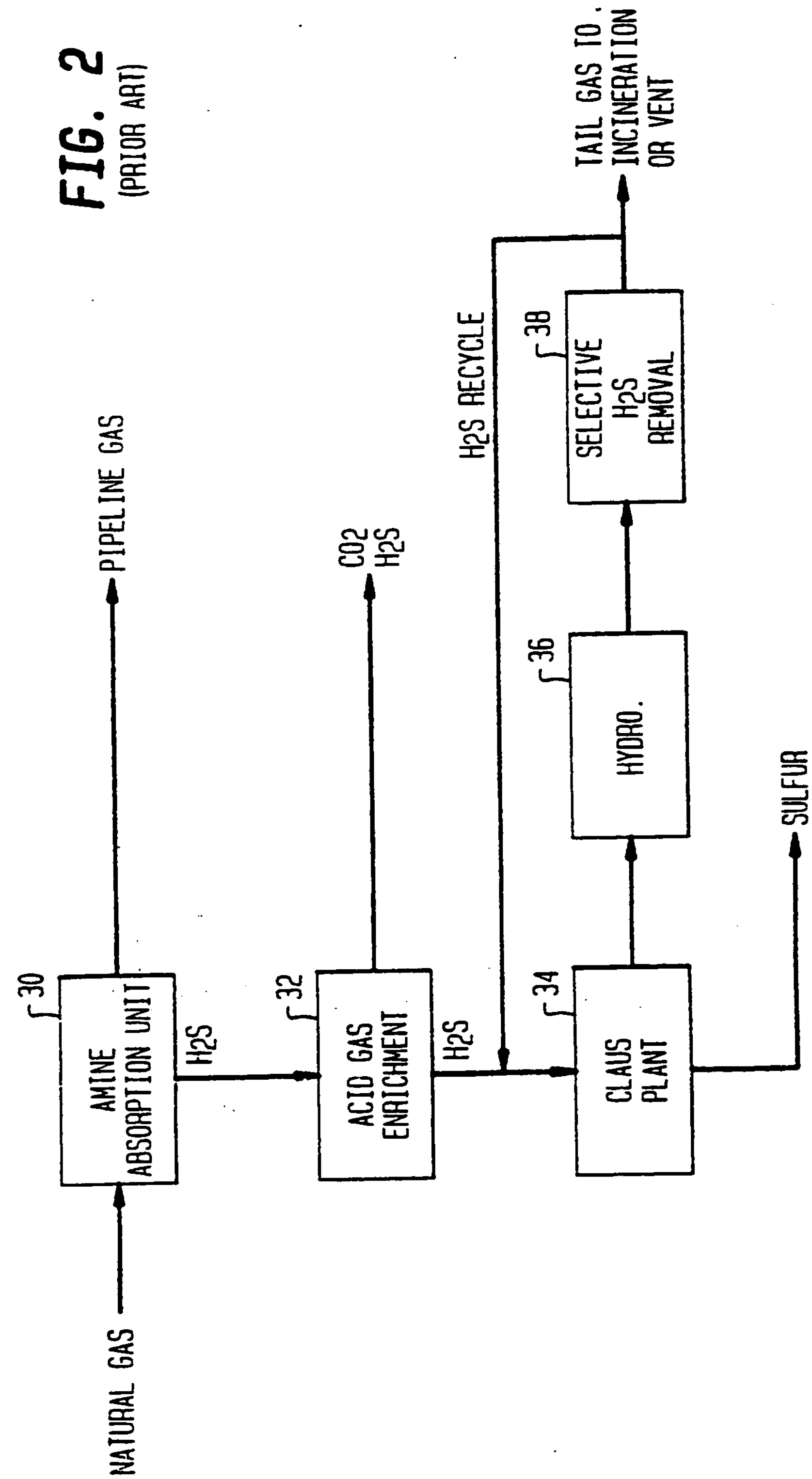



FIG. 2 (PRIOR ART)

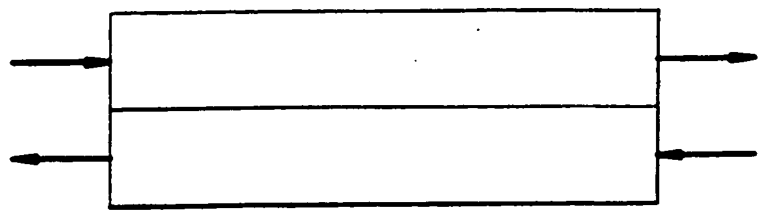


FIG. 3A

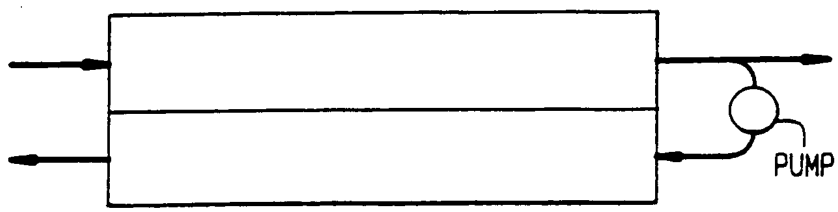



FIG. 3B

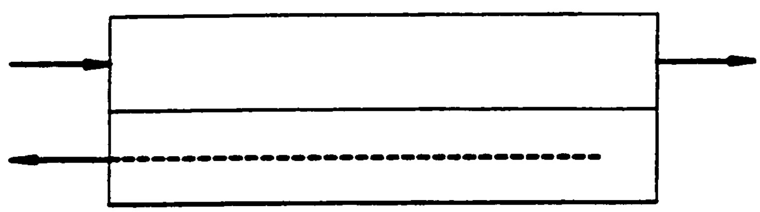


FIG. 3C

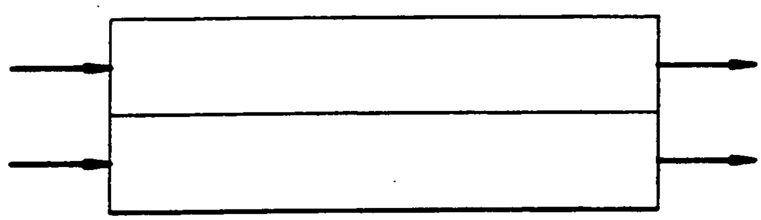


FIG. 3D

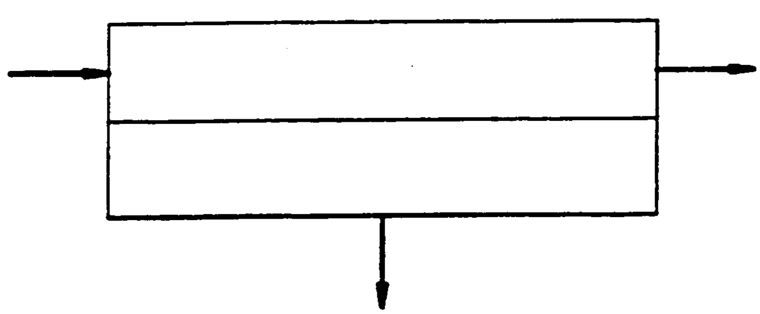


FIG. 3E

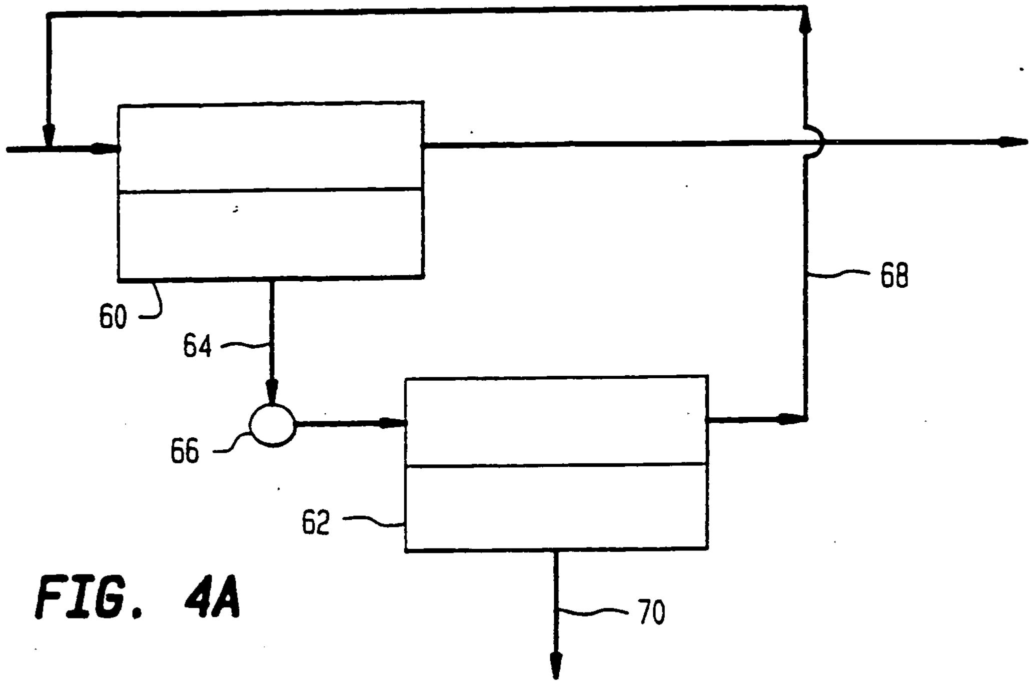



FIG. 4A

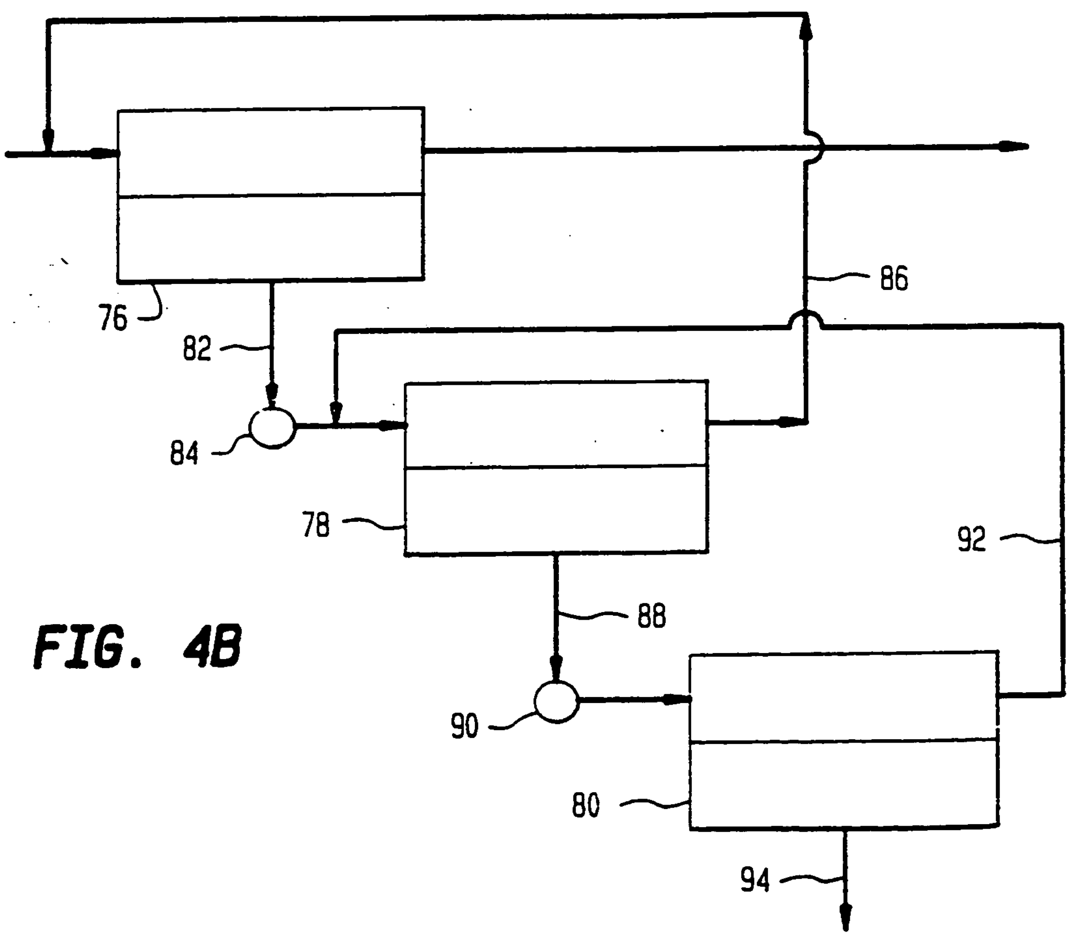
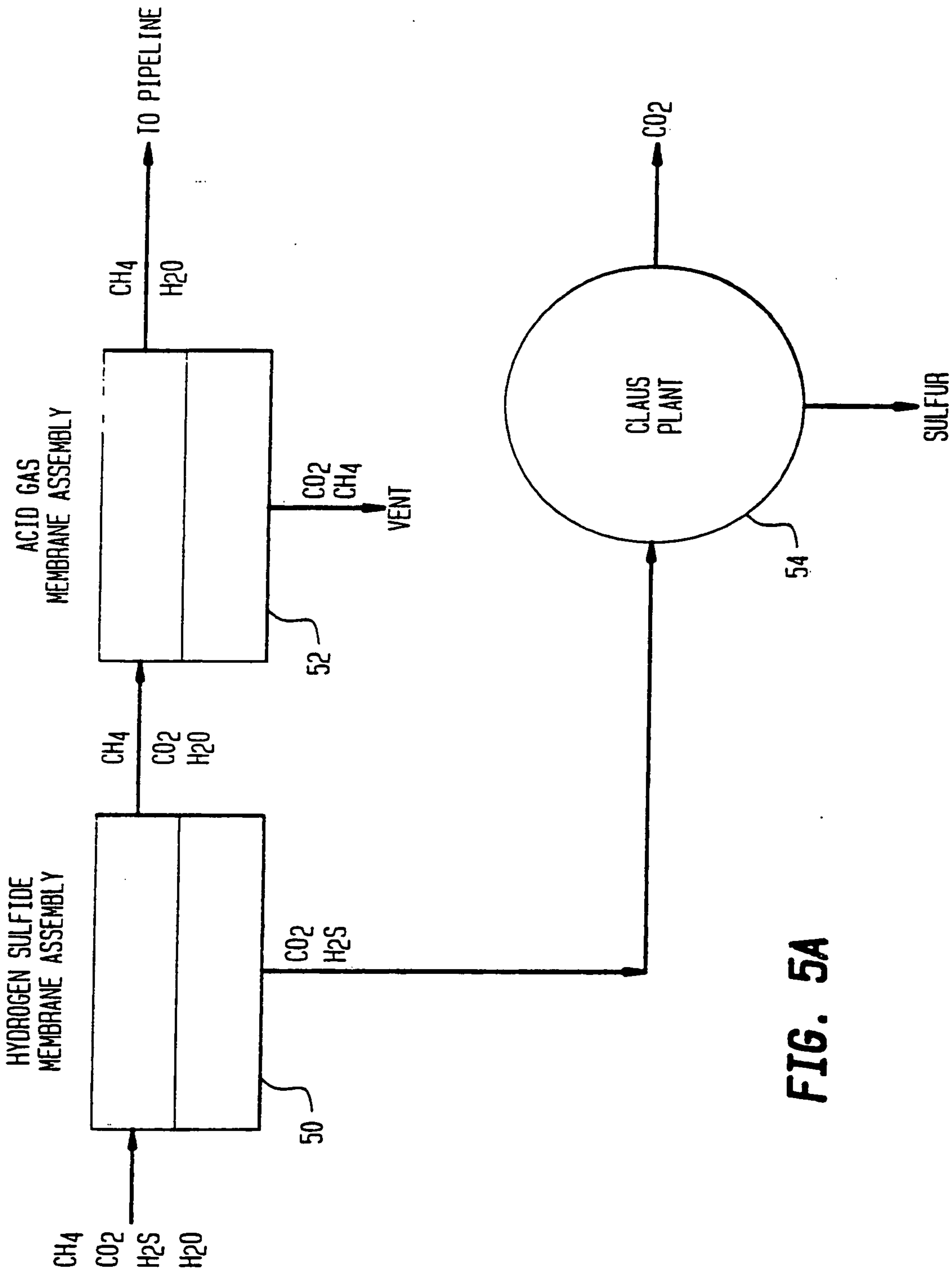



FIG. 4B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54

FIG. 5A

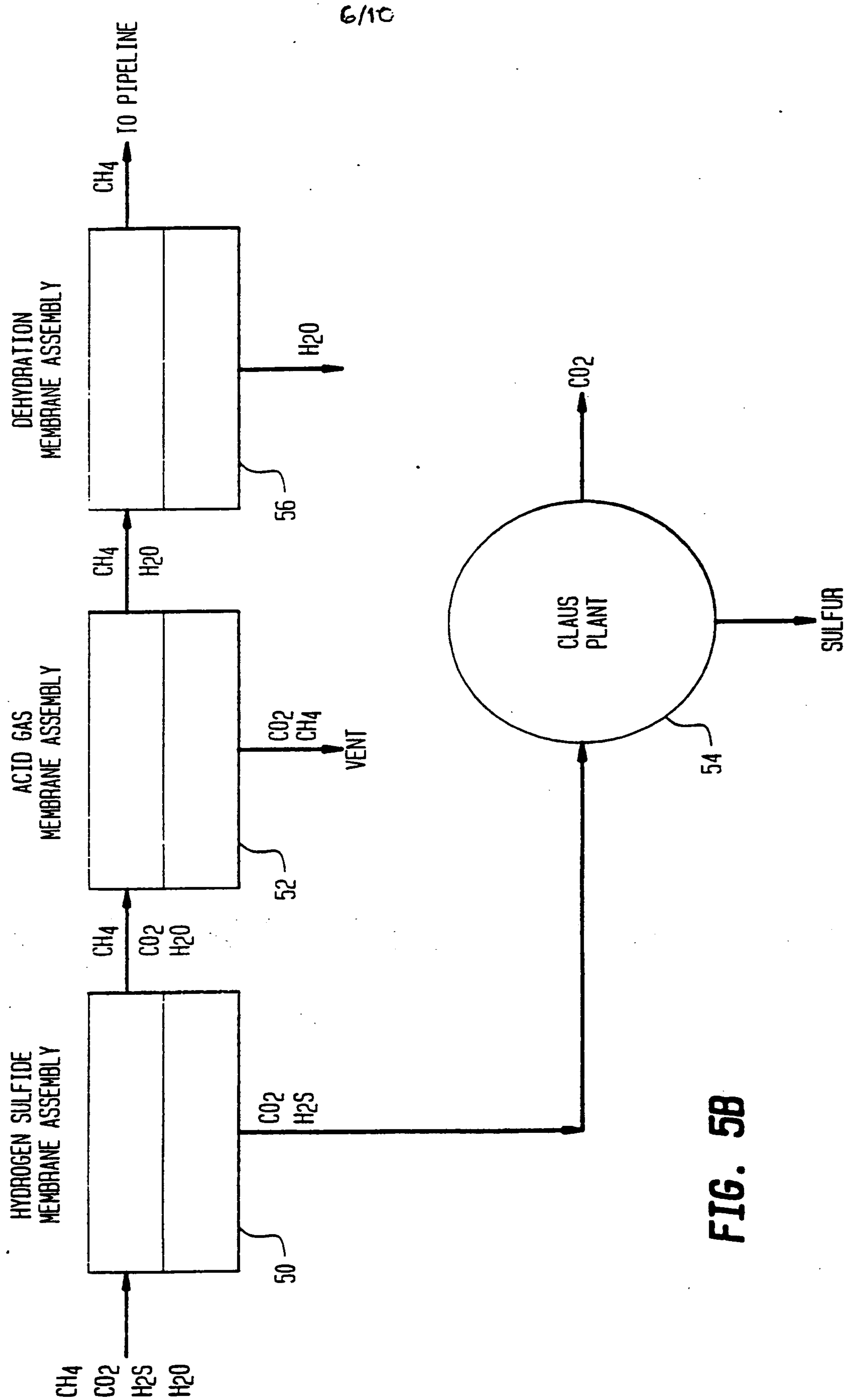
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FIG. 5B

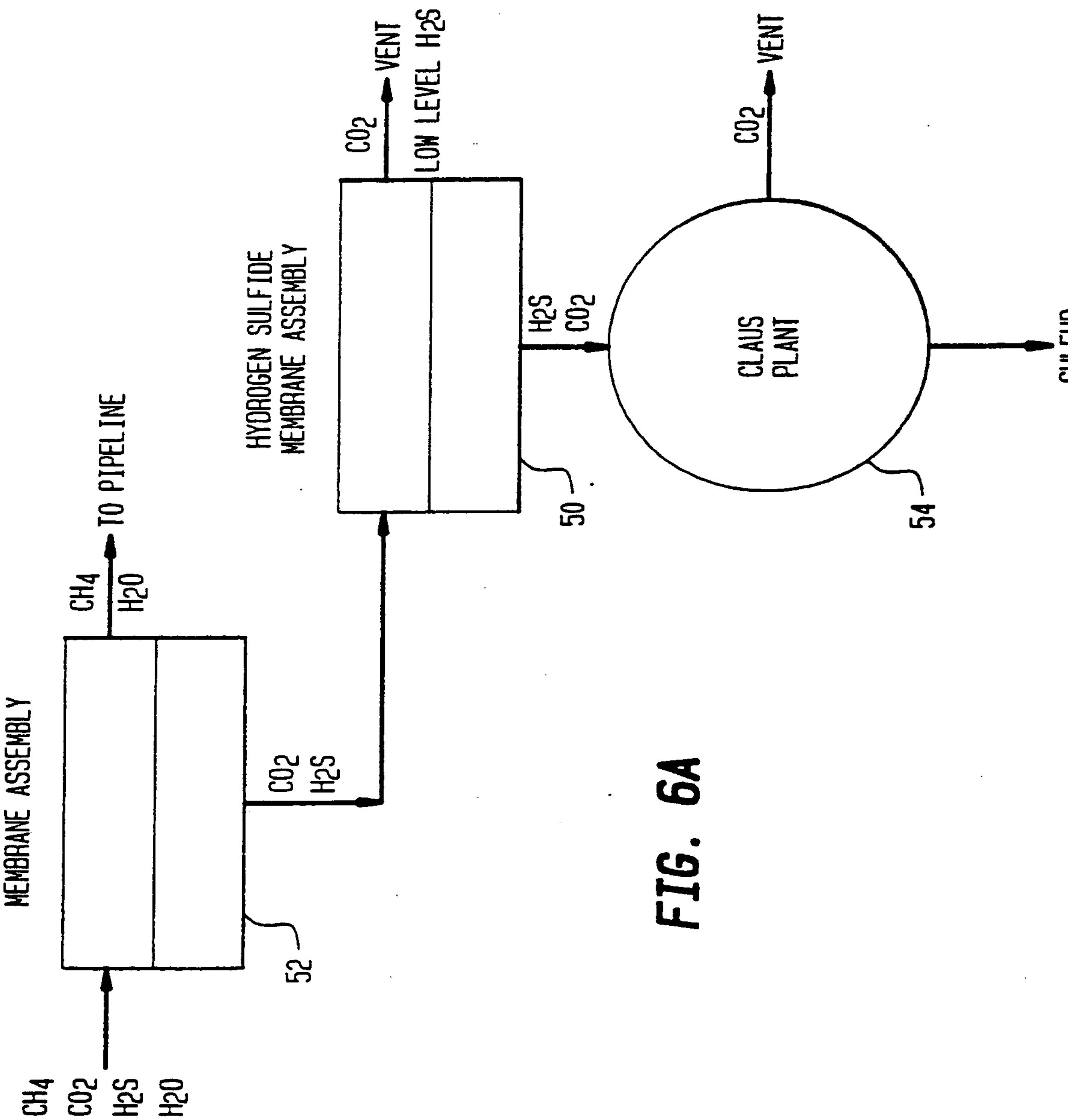
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FIG. 6A

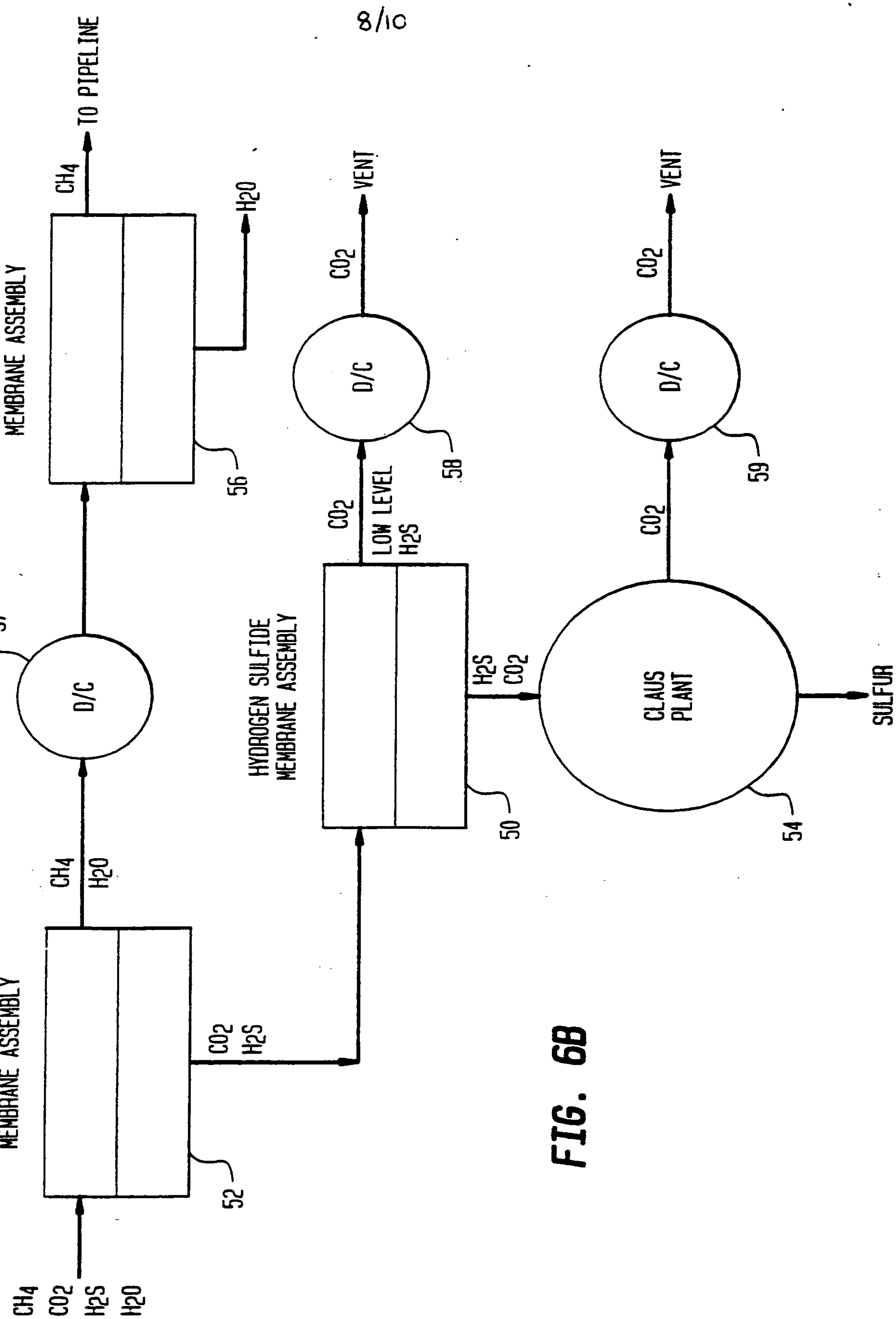
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FIG. 6B

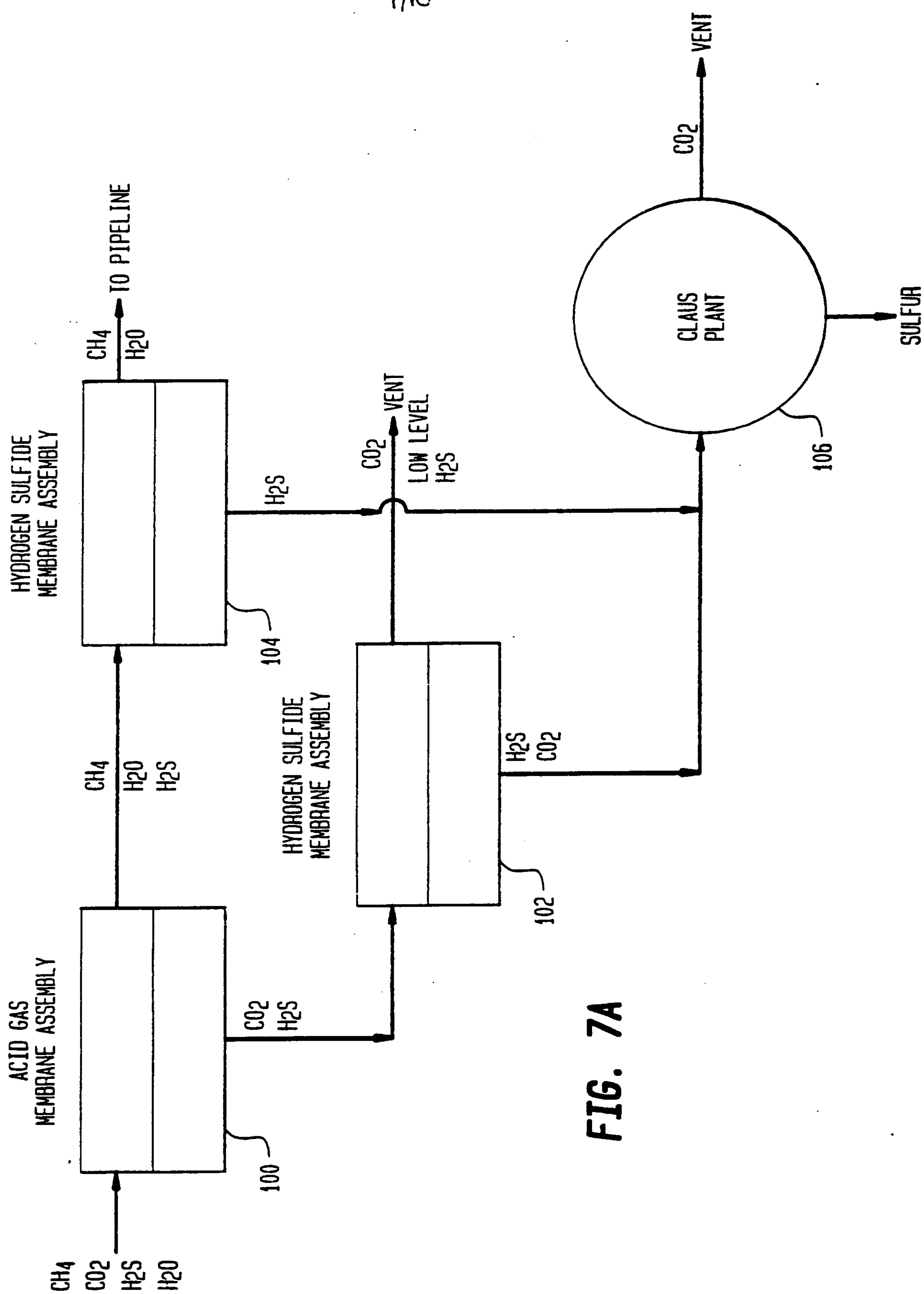

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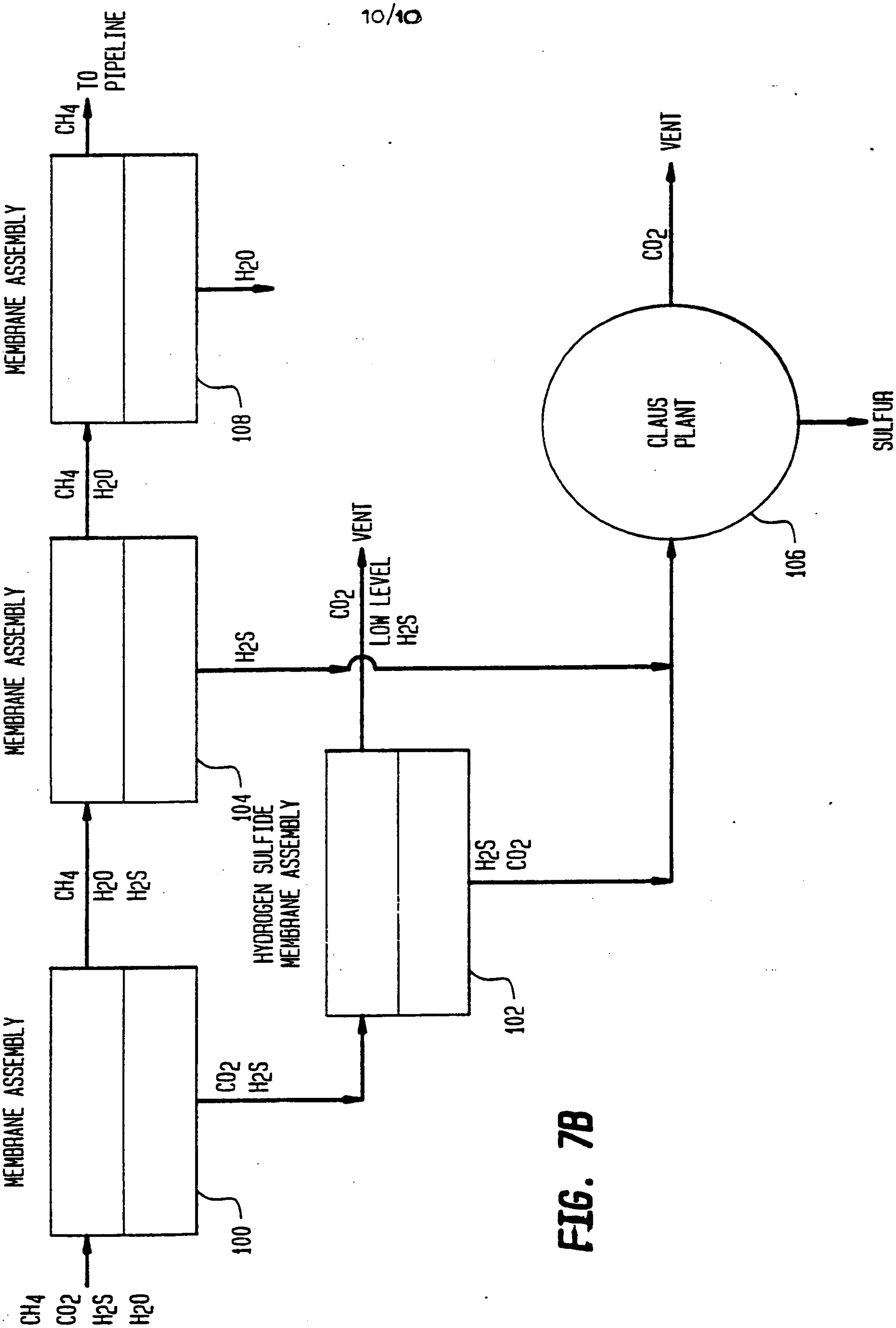
FIG. 7A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PLANT
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FIG. 7B

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/04026

| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6] | |
|---|---|
| According to International Patent Classification (IPC) or to both National Classification and IPC<br>Int.Cl. 5 B01D53/22; C07C7/144 | |

**II. FIELDS SEARCHED**

Minimum Documentation Searched[7]

| Classification System | Classification Symbols |
|---|---|
| Int.Cl. 5 | B01D ; C07C |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

**III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]**

| Category° | Citation of Document,[11] with indication, where appropriate, of the relevant passages[12] | Relevant to Claim No.[13] |
|---|---|---|
| X<br>Y | US,A,4 130 403 (COOLEY ET AL.) 19 December 1978<br>see column 7, line 7 - column 8, line 9; claims 1-17; figure<br>--- | 1,4-11<br>31, 33-40, 45, 47-54, 59,61-68 |
| Y<br>A | US,A,3 534 528 (PORTER) 20 October 1970<br>see the whole document<br>---<br>-/-- | 31, 33-40, 45, 47-54, 59,61-68<br>1,2,4-7, 73,74 |

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

**IV. CERTIFICATION**

| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report |
|---|---|
| 1 02 SEPTEMBER 1992 | 21. 09. 92 |
| **International Searching Authority** | **Signature of Authorized Officer** |
| EUROPEAN PATENT FFICE | CUBAS ALCARAZ J.L. |

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

| Category ° | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No. |
|---|---|---|
| A | GB,A,2 134 814 (COMPAGNIE FRANCAISE DES PETROLES ) 22 August 1984<br><br>see page 5, line 17 - line 32; claim 1<br><br>--- | 1,3, 12-14, 27-29, 41-43, 55-57, 69-72 |

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9204026 SA 60770

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 02/09/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| US-A-4130403 | 19-12-78 | CA-A- 1080133 | 24-06-80 |
| US-A-3534528 | 20-10-70 | None | |
| GB-A-2134814 | 22-08-84 | FR-A- 2540396 | 10-08-84 |
| | | AU-B- 547915 | 14-11-85 |
| | | AU-A- 2408184 | 09-08-84 |
| | | CA-A- 1209489 | 12-08-86 |
| | | DE-A,C 3403635 | 09-08-84 |
| | | FR-A- 2560784 | 13-09-85 |
| | | JP-A- 59193835 | 02-11-84 |
| | | NL-A- 8400308 | 03-09-84 |
| | | US-A- 4497640 | 05-02-85 |

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

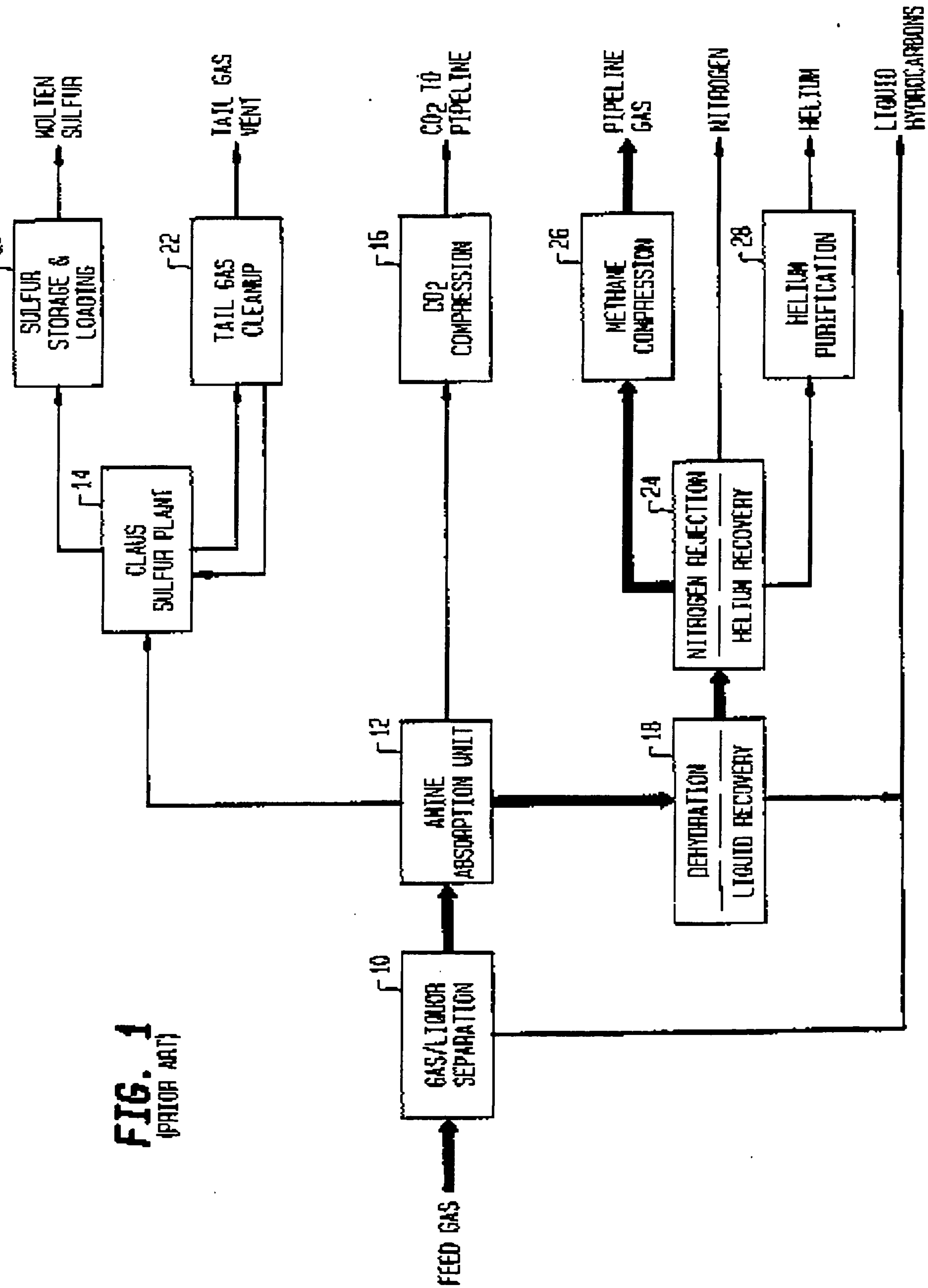


FIG. 1
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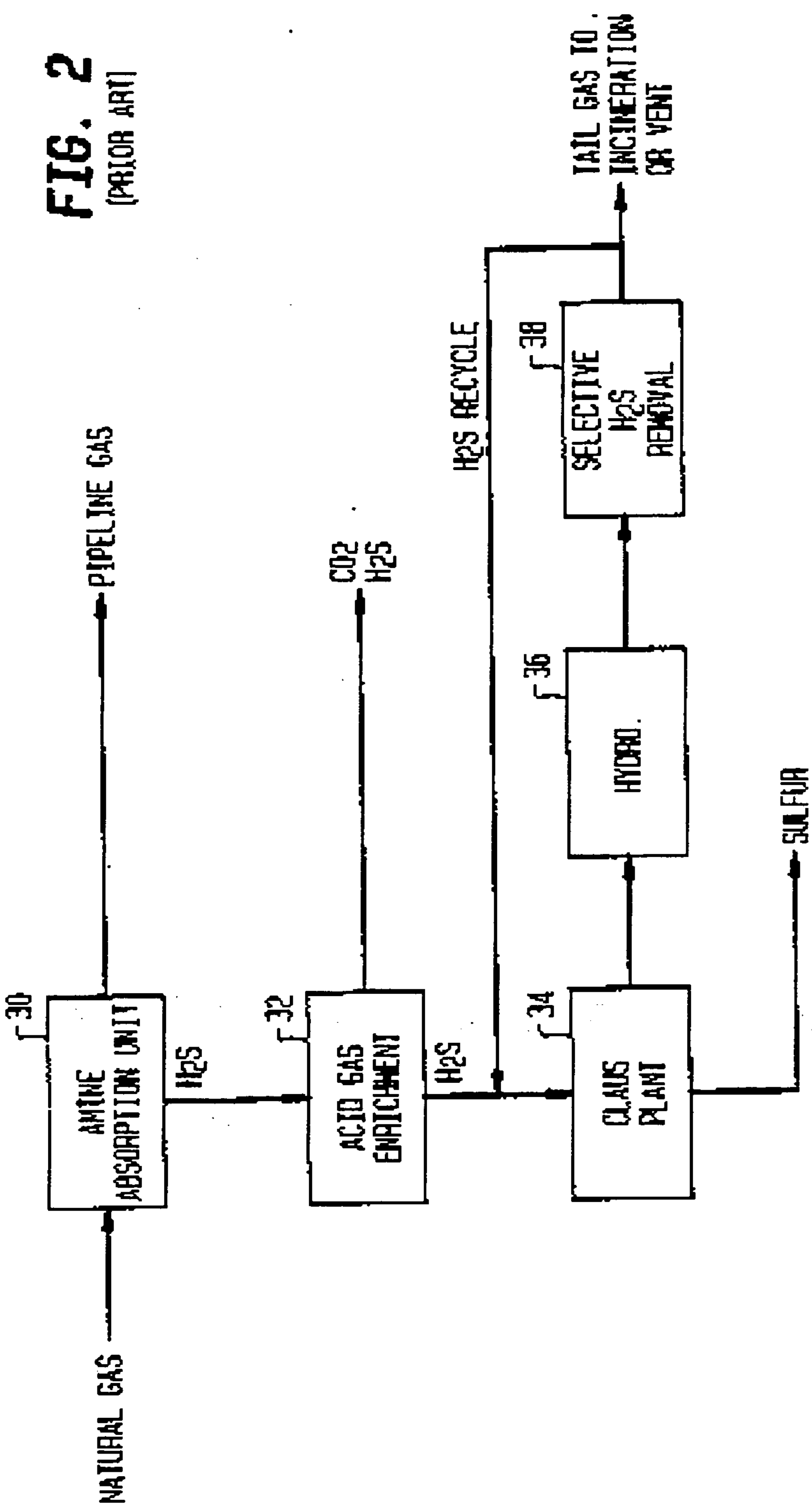


FIG. 2
(PRIOR ART)

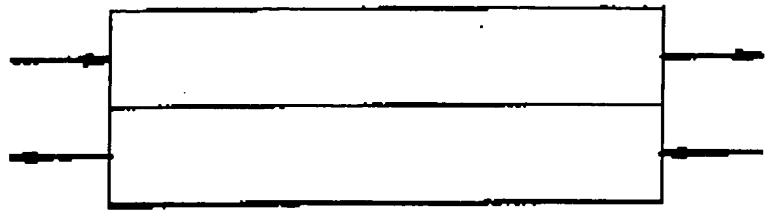

FIG. 3A

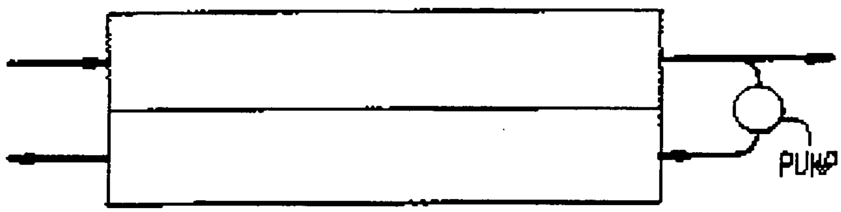


FIG. 3B

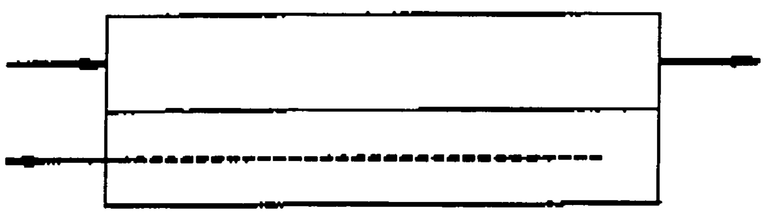

FIG. 3C

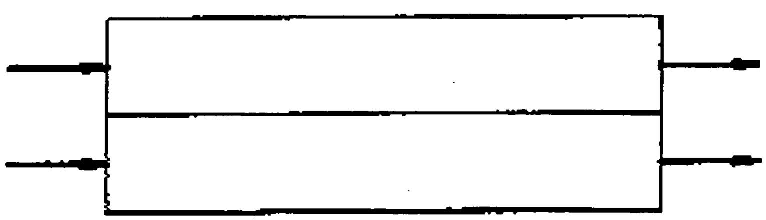

FIG. 3D

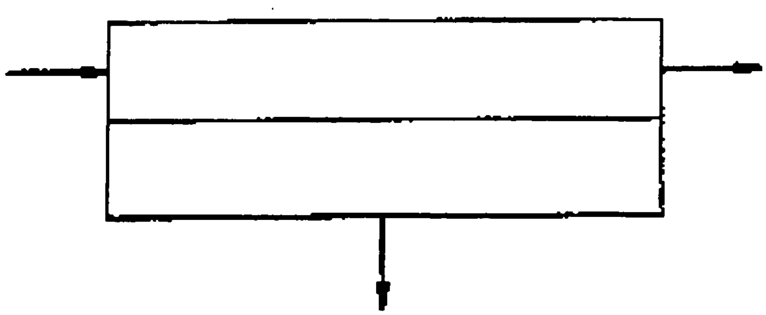

FIG. 3E

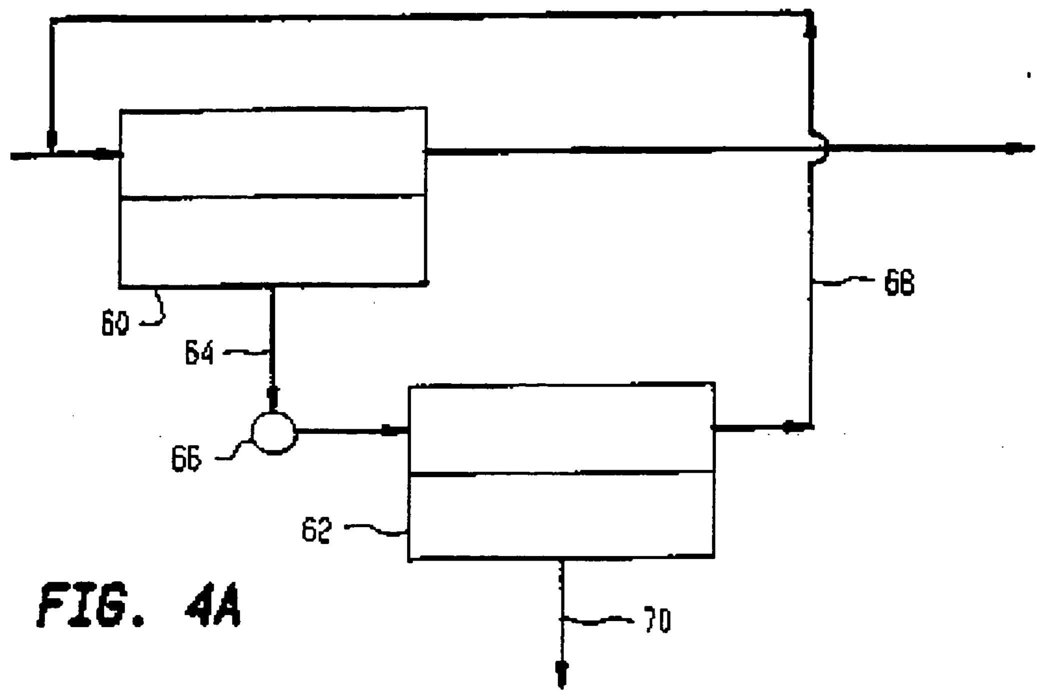


FIG. 4A

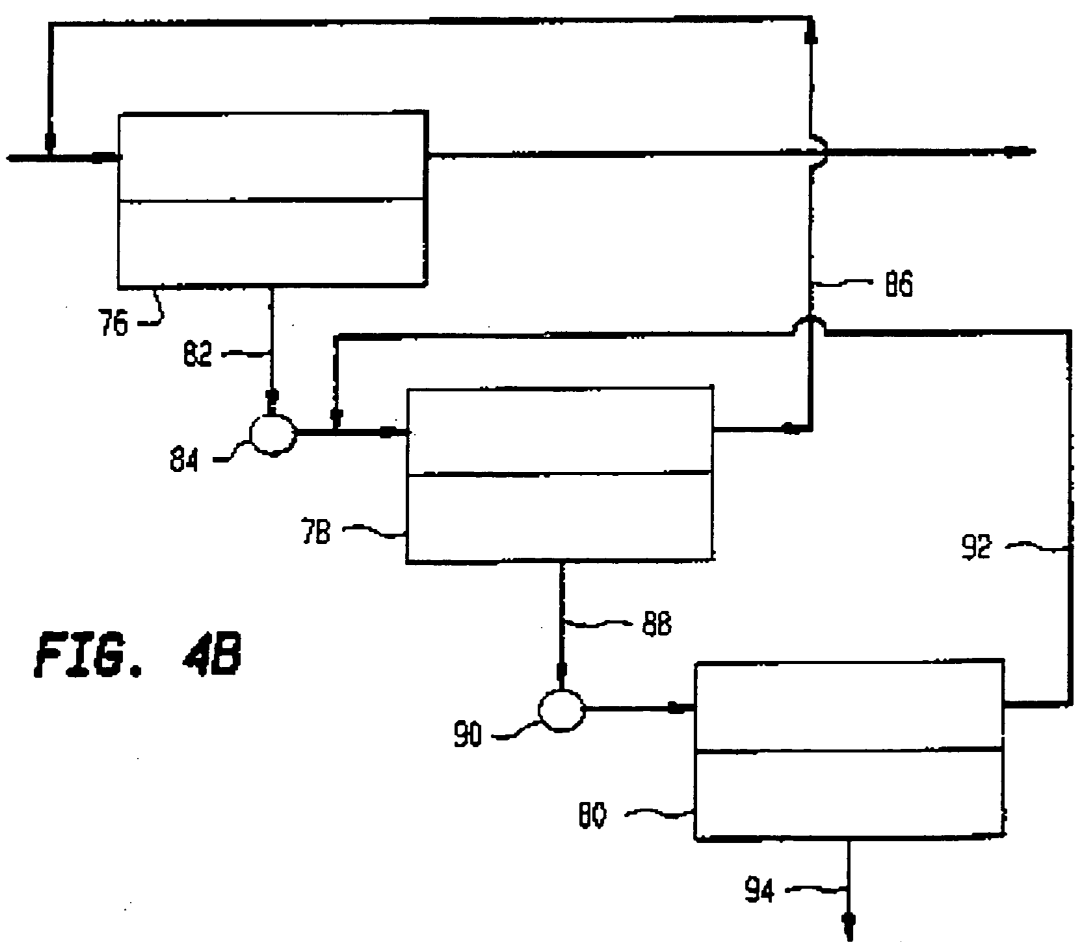


FIG. 4B

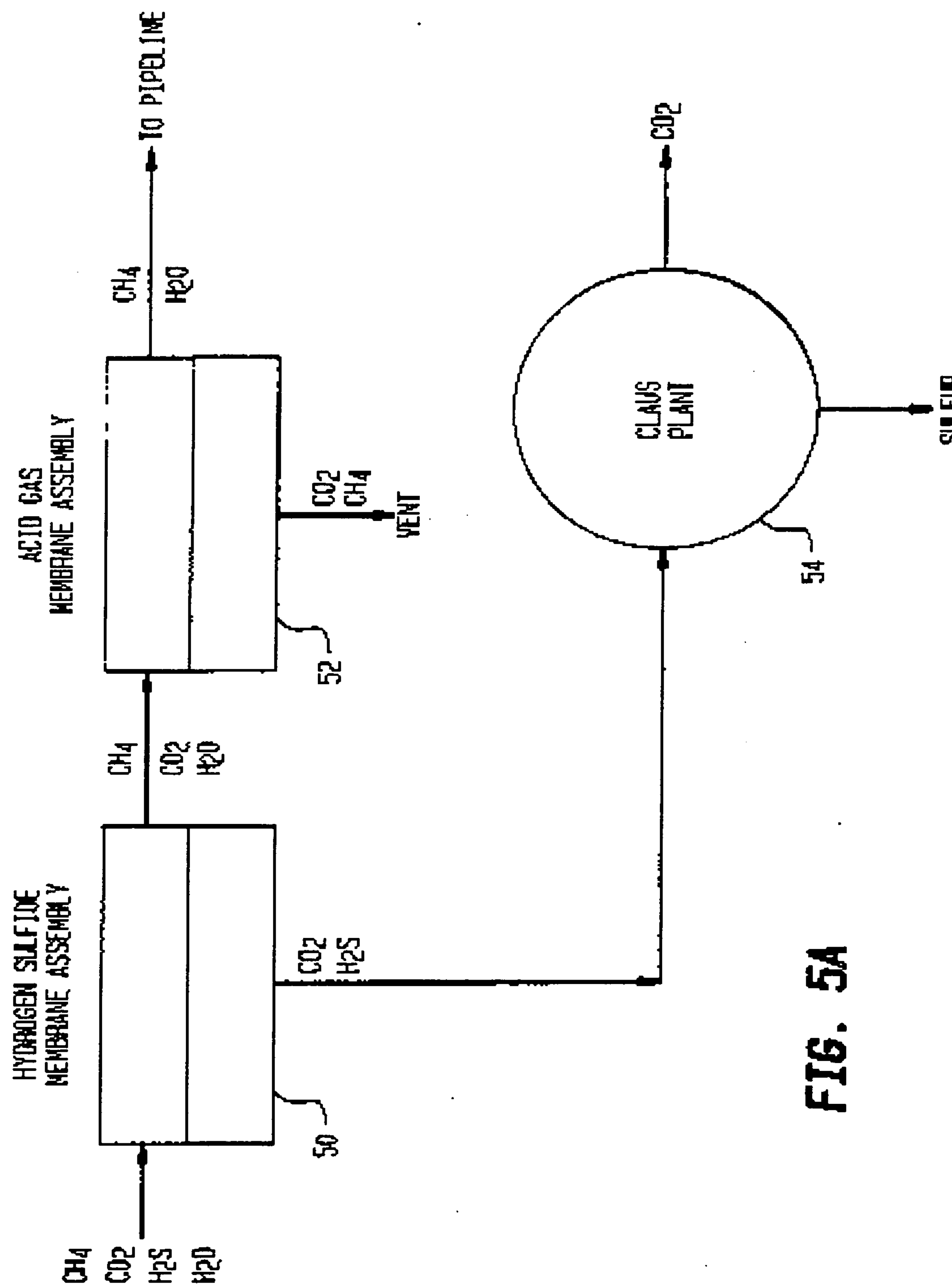
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FIG. 5A

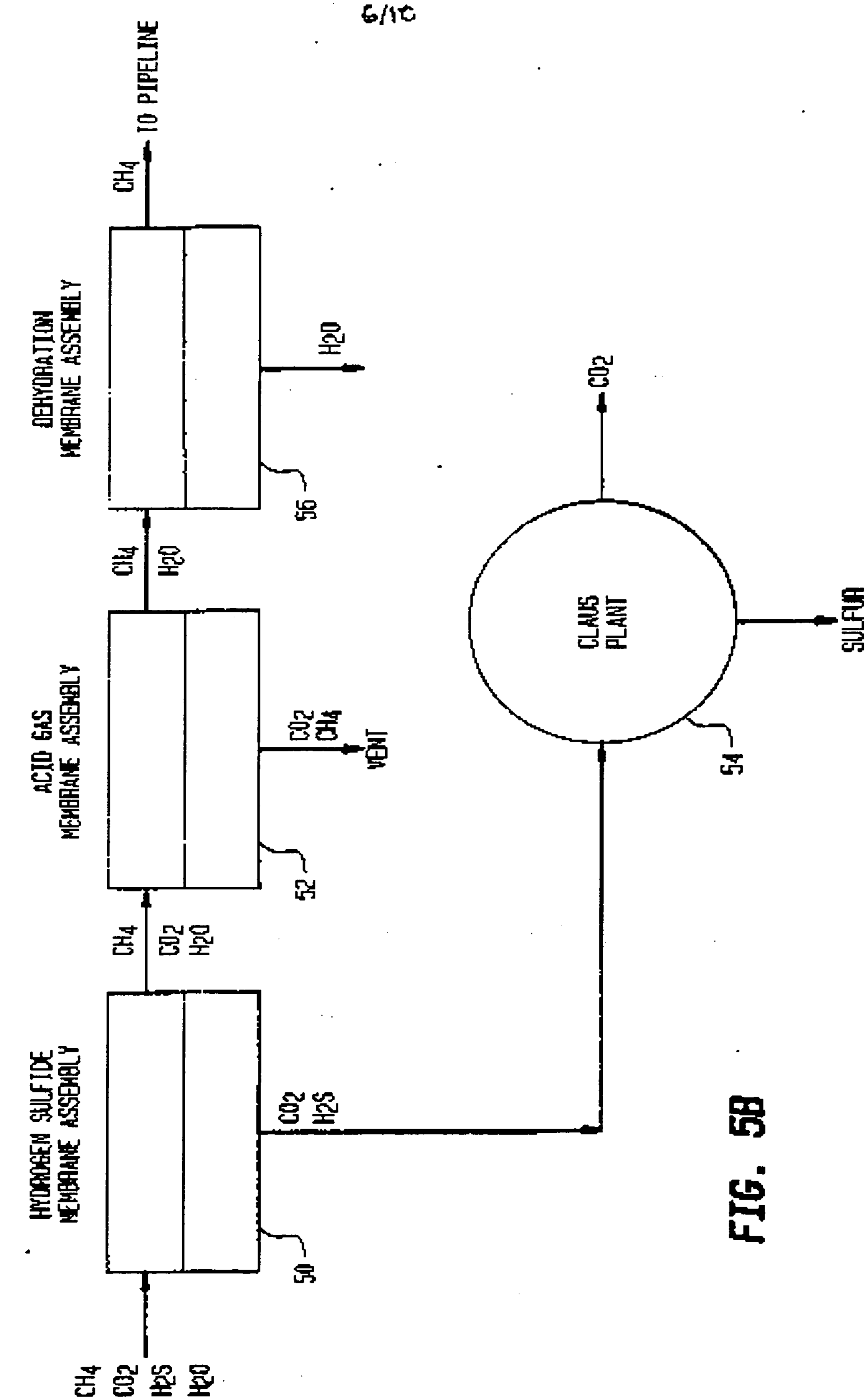
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FIG. 5B

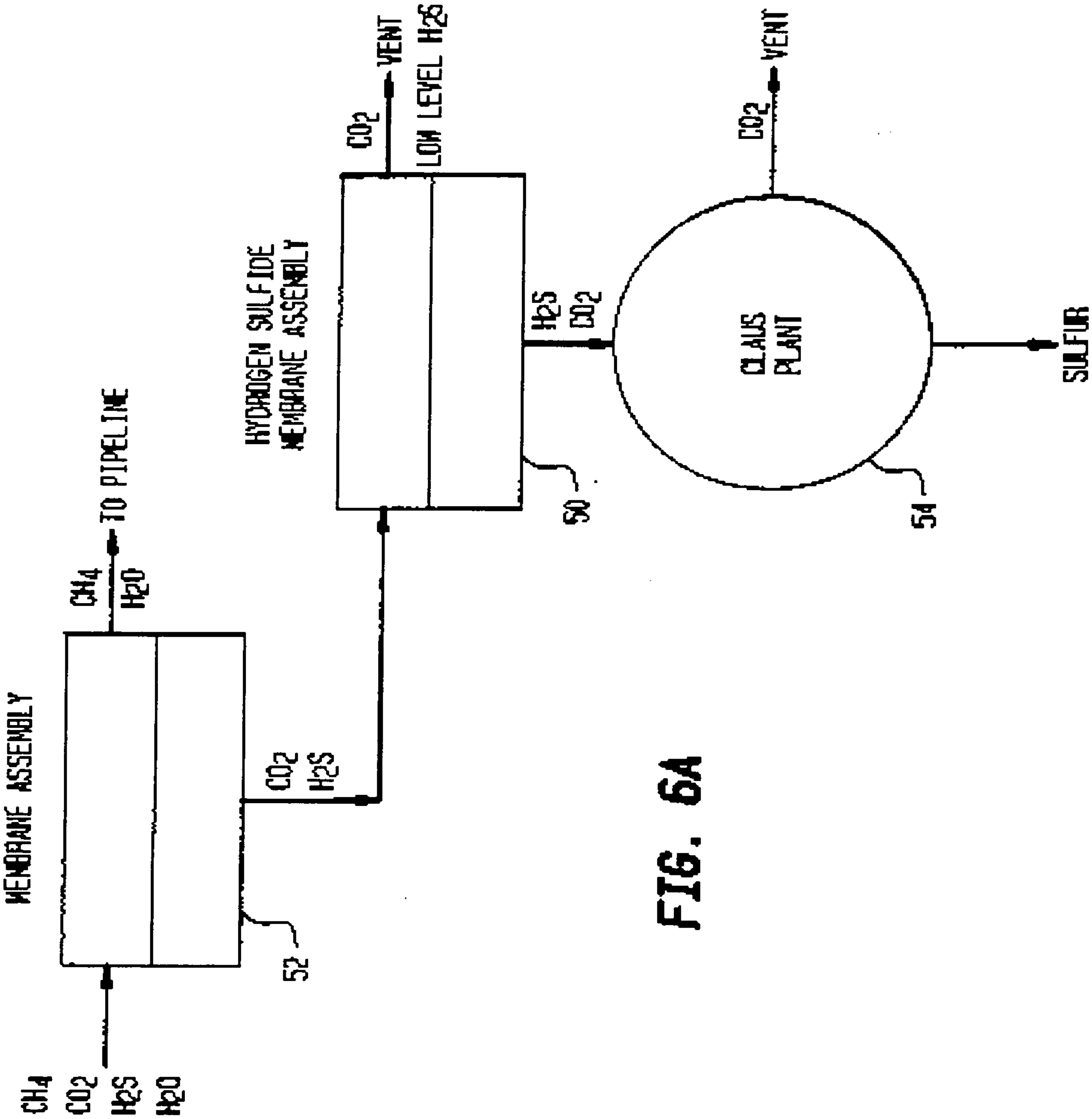
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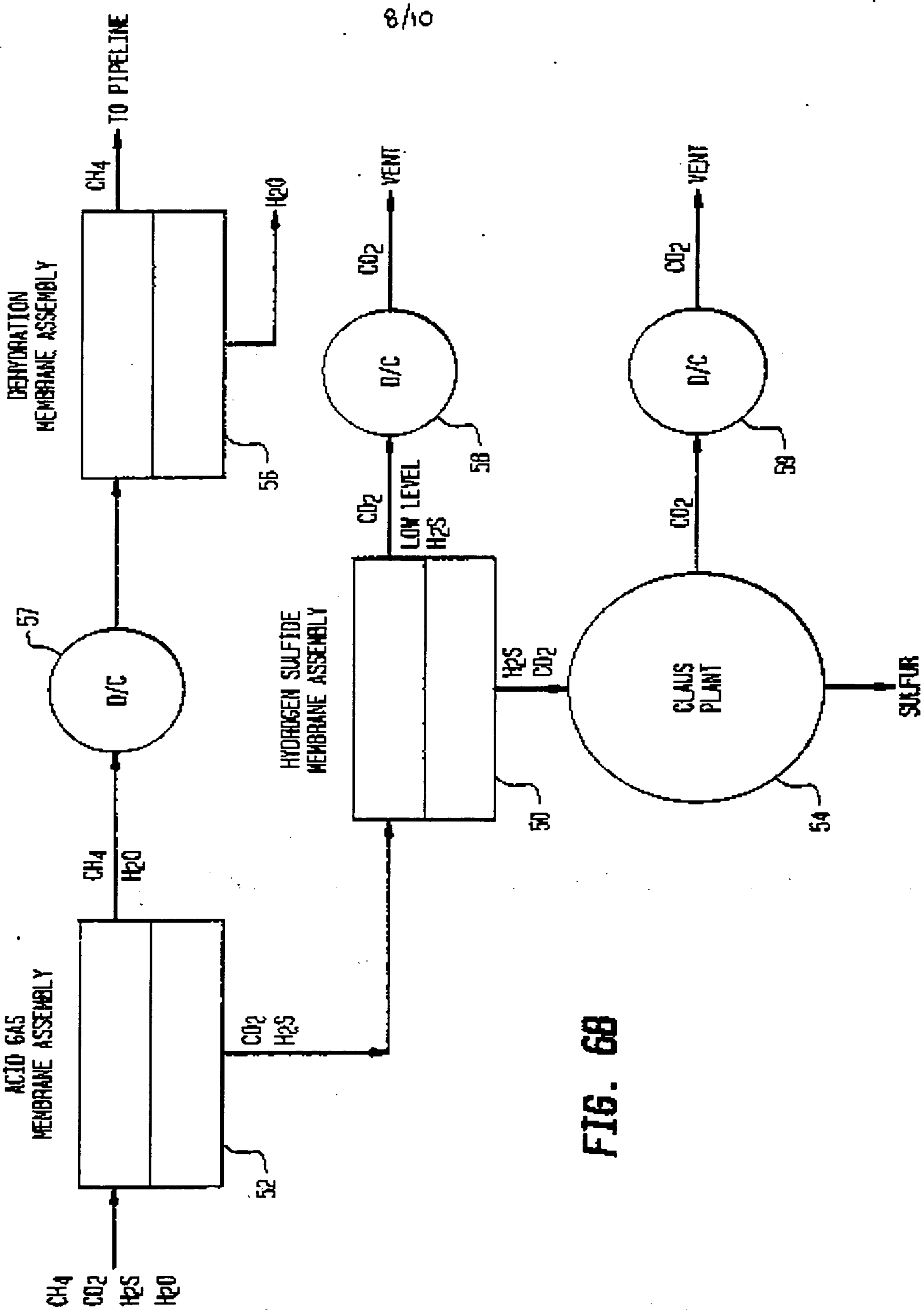
FIG. 6A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VENT

FIG. 6B

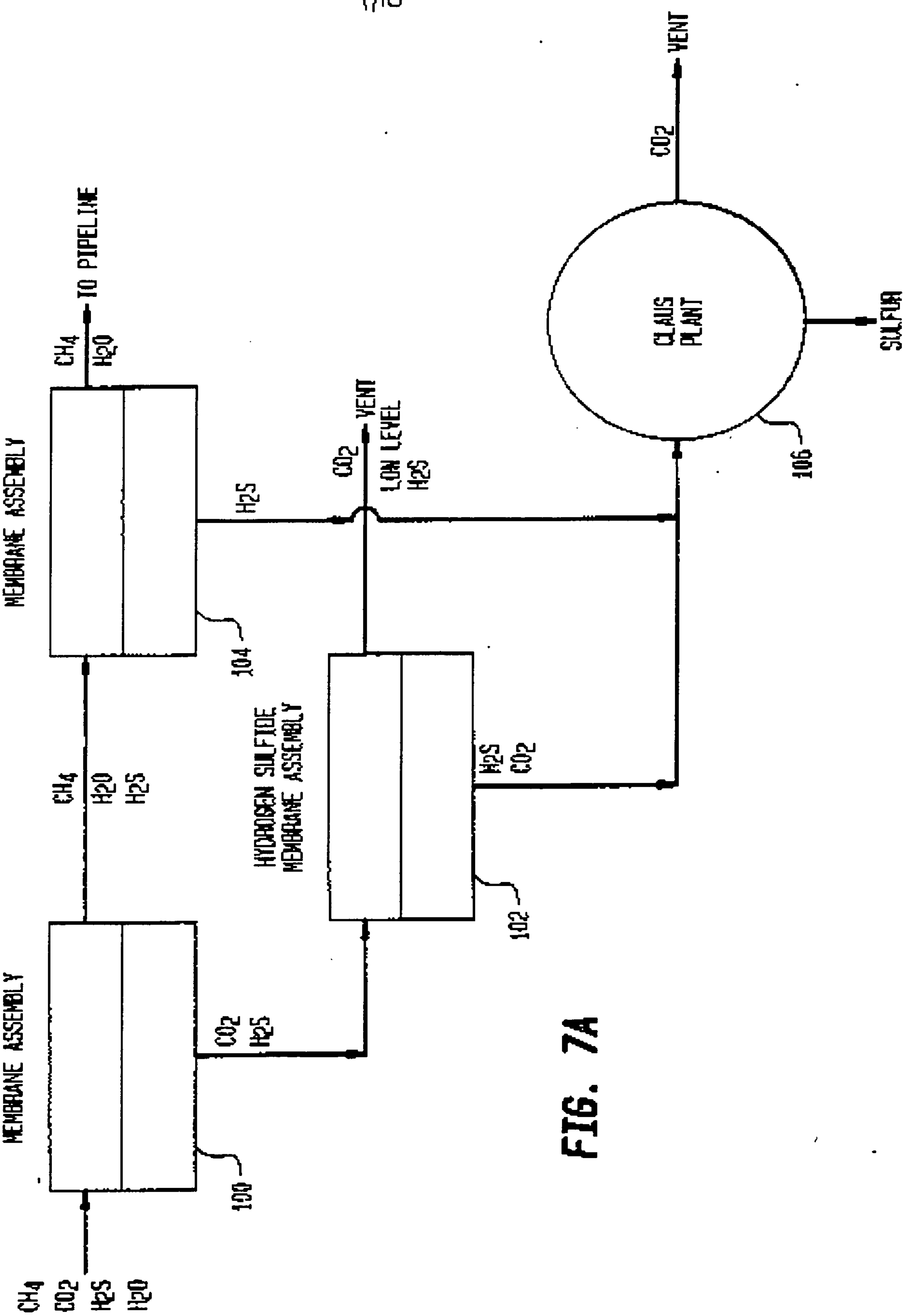
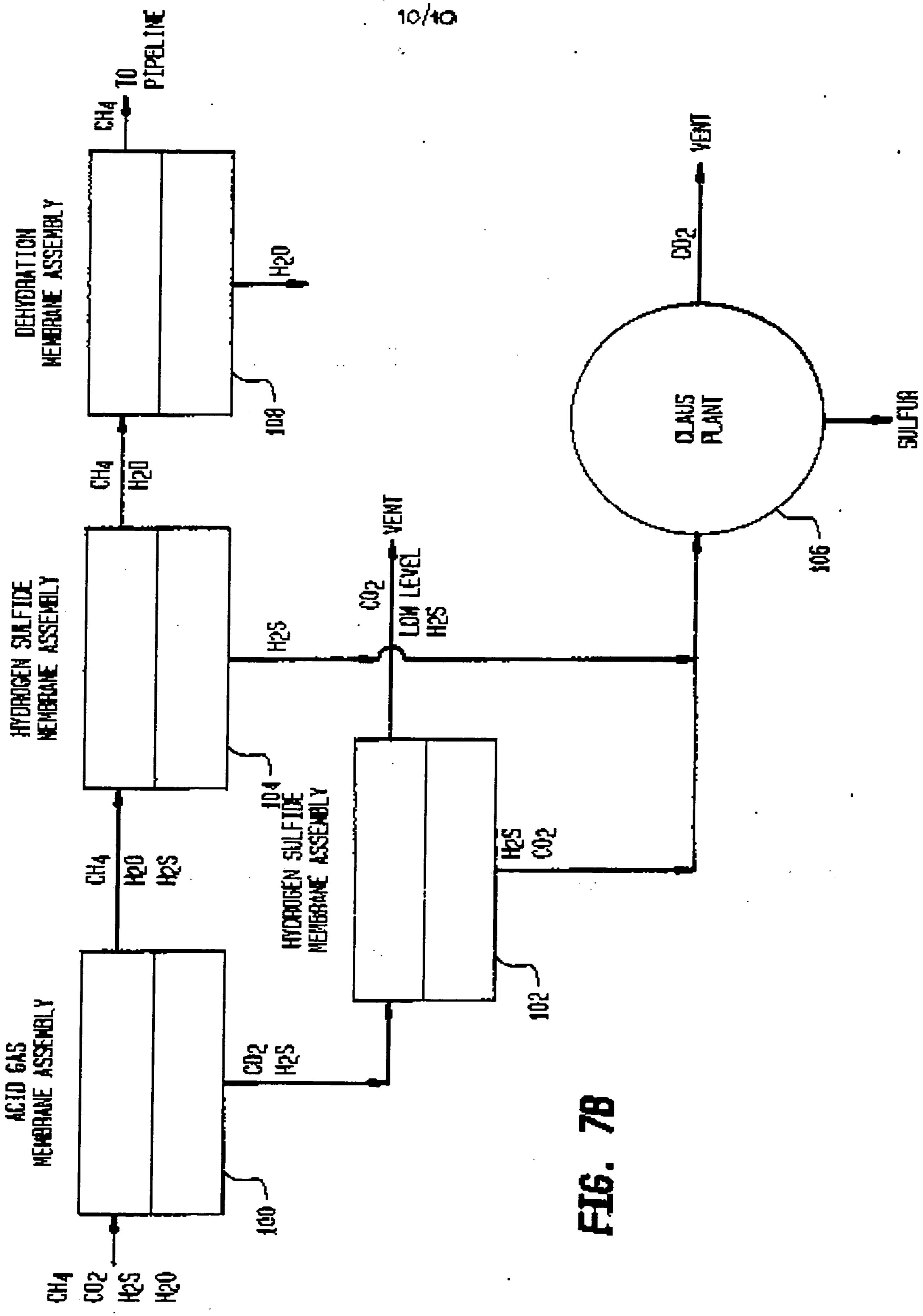

CH4
CO2
H2S
H2O
ACID GAS
MEMBRANE ASSEMBLY
100
CO2
H2S
CH4
H2O
H2S
HYDROGEN SULFIDE
MEMBRANE ASSEMBLY
104
CH4
H2O
TO PIPELINE
H2S
HYDROGEN SULFIDE
MEMBRANE ASSEMBLY
102
H2S
CO2
CO2
LOW LEVEL
H2S
VENT
CLAUS
PLANT
106
SULFUR
CO2
VENT

FIG. 7A



CH4
CO2
H2S
H2O
ACID GAS
MEMBRANE ASSEMBLY
100
CO2
H2S
CH4
H2O
H2S
HYDROGEN SULFIDE
MEMBRANE ASSEMBLY
102
H2S
CO2
CO2
LOW LEVEL
H2S
VENT
HYDROGEN SULFIDE
MEMBRANE ASSEMBLY
104
H2S
CH4
H2O
DEHYDRATION
MEMBRANE ASSEMBLY
108
H2O
CH4
TO
PIPELINE
CLAUS
PLANT
106
SULFUR
CO2
VENT


FIG. 7B